A THESIS ON

BUTYL TITANATE,

PREPARATION, PROPERTIES AND APPLICATIONS

BY

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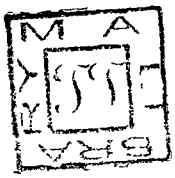

A C K N O W L E D G E M E N T S

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P R E F A C E

The applications of butyl titanate in the paint and allied industries have been developed considerably in the last twenty years but very little attention has been given to the theoretical aspects of these problems. The author, therefore, undertook a complete study of the properties of butyl titanate which have a direct bearing on its applications in thermostable coatings, thixotropic paints and as a polymerisation catalyst.

The thesis consists of three parts. In part I the preparation and properties of butyl titanate are described. Part II deals with butyl titanate as a polymerising agent for linseed oil. Applications of butyl titanate in thermostable coatings and thixotropic paints are discussed in Part III of the thesis.

Preparation of titanium tetrachloride, the starting material and that of butyl titanate is described. Optimum conditions for preparation of titanium tetrachloride using titanium dioxide and coke were determined and mechanism of the reaction between chlorine and titanium dioxide and the part played by coke in this reaction was studied. Conditions for synthesis of pure butyl titanate were established.

The reported information on physico-chemical properties of alkyl titanates being meagre, detailed study of ultraviolet and infrared absorption spectra and

of structural changes as a result of thermal treatment, was made. Spectrophotometric grade reagents were prepared for this study. Ultraviolet absorption studies were made for the first time. Although the absorption peak in both the cases was observed to be at 237 millimicrons, it was sharp in butyl alcohol but broad in ethyl alcohol. Beer's law was obeyed suggesting the possibility of using this method for the estimation of butyl titanate. Experiments were done for determining butyl titanate in linseed oil. The molecular extinction coefficients in butyl alcohol and ethyl alcohol were approximately 9300 and 8000 respectively.

The infrared absorption spectrum of butyl titanate showed characteristic peaks in the region 5.9, 6.7 and 8.4 microns due to C-O, Ti-O-C and Ti-O groups. A peak observed at 13.3 microns was assigned to O-Ti-O group.

A detailed study of thermal behaviour of the hydrolysate of butyl titanate was undertaken with a view to obtain evidence for the formation of brookite, one of the three crystalline forms of titanium dioxide which is available only in nature and it is reported that it can be prepared by hydrolysis of alkyl titanates. Endothermic peaks due to loss of loosely held water and water of hydration and exothermic peaks as a result of various structural changes taking place were observed. A new exothermic peak at 315°C was observed in the thermogram

of the hydrolysate of butyl titanate. This was not reported by the earlier workers in the differential thermal analysis curves of the hydrated titanium dioxide. The changes were further followed up by X-ray diffraction studies. The study showed that butyl titanate when hydrolysed and heated yields anatase.

The suitability of butyl titanate as a catalyst for the polymerisation of linseed oil which is a major oil used in paint industry was thoroughly investigated. The extent and nature of polymerisation was followed by changes in viscosity, colour, refractive index and ultraviolet and infrared absorption spectra.

It was observed from the viscosity data that the polymerisation in presence of butyl titanate takes place in two stages. The rate of change of viscosity indicates that polymerisation is linear in the first stage followed by three dimensional polymerisation in the second stage. In some cases there is time lag between the two stages.

The higher polymer formation is related to double bond functionality of the linseed oil. Viscosity data indicates that effective double bond functionality is maximum on addition of 0.2 percent butyl titanate and decreases with increase in proportion of the titanate. This is explained assuming dimerisation by addition of conjugated double bond to a non-conjugated double bond resulting in lower double bond functionality than if

dimerisation takes place by addition reaction between two conjugated double bonds. The examination of ultra-violet and infrared absorption spectra of polymerised product shows that polymerisation at the conjugated trans-trans bonds is instantaneous but that at the iso-lated trans bond it is slow. The cis-cis conjugated bonds are not polymerised and as a result the product shows preponderance of cis-cis conjugated double bonds. Butyl titanate has oxidising action on the oil when used in higher proportions and on heating for longer duration, with consequent increase in colour. Addition of 0.2 percent butyl titanate and heating at 250°C for 10 hours is recommended to get a polymerised oil having satisfactory colour and viscosity.

Application of butyl titanate in thermostable coatings was studied. When used with aluminium paint it was observed that even 0.1 percent butyl titanate was sufficient to give desired adhesion of paint with the underlying surface which improved on further exposure to heat at high temperature without forming any blister or peeling off of the paint film as was observed in case of the paint without butyl titanate.

A detailed study of the use of butyl titanate as a promotor of thixotropy in the paint formulations using rutile and anatase and linseed oil, showed that the paints which are non-thixotropic completely change

to thixotropic paints in presence of butyl titanate. The sol to gel and gel to sol transformation of the paint an essential feature of the thixotropic system was followed by viscosity changes.

When butyl titanate is added to a non-thixotropic paint containing rutile or anatase and linseed oil, a part of butyl titanate hydrolyses to form titanium hydroxide which being more reactive than the titanium dioxide pigment, gets adsorbed on the pigment particles and stabilises the titanium dioxide sol. Butyl titanate also induces gel formation. It dissociates weakly into butyl and titanate ions. While butyl ions have affinity for linseed oil and remain dispersed in the oil, titanate ions are attracted towards pigment particles. Due to the weak dissociating nature of butyl titanate butyl ions are not very far removed from titanate ions and remain in the neighbourhood of pigment particles along with the oil molecule. Thus butyl titanate acts as a link between pigment and vehicle oil. Since titanium ion is tetravalent, at least four linseed oil poly molecules are associated with each pigment particle when only one butyl titanate molecule is adsorbed on them. The oil thus loses its mobility and the system becomes viscous. When stress is applied, the system is disturbed, titanate and butyl ions are separated and the oil gains its mobility, the viscosity decreases and gel to sol transformation takes place. 0.5 percent butyl

titanate was observed to be optimum for obtaining the desired thixotropy.

Thus the above study gives an insight into the part played by butyl titanate in the catalytic polymerisation of linseed oil and thixotropy of rutile and anatase paints.

SUMMARY

The applications of butyl titanate in the paint and allied industries have been developed considerably in the last twenty years but very little attention has been given to the theoretical aspects of these problems. The author, therefore, undertook a complete study of the properties of butyl titanate which have a direct bearing on its applications in thermostable coatings, thixotropic paints and as a polymerisation catalyst.

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PART I

PREPARATION AND PROPERTIES OF BUTYL TITANATE

INTRODUCTION

Organic compounds of titanium[1] are confined almost entirely to those in which carbon is linked to titanium via an oxygen atom; although there are isolated instances of compounds with titanium-carbon bonds, which are unstable and as yet of no practical interest. The former type may be designated as titanium esters, derived from the hypothetical ortho-titanic acid $Ti(OH)_4$ or may be considered as alkoxides of tetravalent titanium.

It is important to realise that there is no similarity either in structure or properties between titanium esters and the silicones, because of the absence of titanium-carbon bond in the former compounds. If an analogy is desired, it is between the use of esters of titanium and those of silicon.

Titanium esters

Some of the physical properties of the ortho-esters of titanium are given in Table 1.

Table 1

Physical Properties of Alkyl Ortho-Titanates

R*	Yield %	B.P. °C/mm. Hg	n^t_D/°C	d^t_4/°C
C_2H_5	66.0	104/1.0	1.5051/35	1.107/35
n-C_3H_7	42.0	170/3.0	1.4803/35	0.997/35
n-C_4H_9	49.7	134-136/0.5-1.0	1.4063/35	0.9927/35
iso-C_4H_9	68.8	141/1.0	1.4749/54	0.9750/35
sec-C_4H_9	40.0	90-92/0.5-1.0	1.455/35	0.9196/35
ter-C_4H_9	45.0	62-63/1.0	1.4436/20	0.8893/20
n-C_8H_{17}	63.3	219/1.0	1.4762/35	-

R* = alkyl radical

In general, titanium esters are rather viscous, yellowish liquids, with high boiling points with the exception of methyl ester which is solid. At atmospheric pressure decomposition occurs below the boiling point, but distillation can be effected under reduced pressure. The esters are completely miscible with almost all anhydrous organic solvents, oil, etc., although certain polymerised drying oils are an exception.

The methyl ester is exceptional in being a solid which tends to sublime with decomposition at high temperature. It is insoluble in most solvents and only sparingly soluble in alcohols. The difference is explained on the basis of the small molecule of methyl titanate allowing considerable association, whereas the higher esters are restricted to association to dimers and trimers.[2] Ethyl and iso-propyl titanates, normally liquids, tend to deposit crystals on standing which rapidly melt on heating. No tendency to solidification is observed in other esters upto C_{12}, above which the esters are waxy solids.

The esters react with almost all compounds containing hydroxyl groups. There is stepwise replacement of the alkoxy groups (I); with water the ultimate product is titanium dioxide (II). This, however, only occurs when there is a considerable excess of water present. It has been shown that at least two of the alkoxy groups can be readily hydrolysed, the other two are more firmly bonded. With small amounts of water hydrolysis of the first one or two alkoxy groups occurs (III). Condensation can then

occur especially on heating (IV).

$$Ti(OR)_4 + R'OH = Ti(OR)_3.OR' + ROH \quad I$$

$$Ti(OR)_4 + 4H_2O = TiO_2.2H_2O + 4ROH \quad II$$

$$Ti(OR)_4 + H_2O = Ti(OH)(OR)_3 + ROH \quad III$$

$$2Ti(OH)(OR)_3 = (RO)_3\ Ti\text{-}O\text{-}Ti(OR)_3 + H_2O \quad IV$$

The released water will then affect further hydrolysis, which results in the formation of larger condensates. The rate of hydrolysis of titanium esters derived from aliphatic alcohols decreases with increasing molecular weights, although certain esters are exceptionally resistant to hydrolysis e.g. iso-octyl titanate.

Till 1940, organic titanium compounds attracted very little attention. A change was, however, brought by the work carried out by Australian workers who were the first to suggest practical uses for alkyl titanates. The rate of hydrolysis of titanium esters derived from aliphatic alcohols decreases with increasing molecular weight. But in case of normal butyl ester the rate of hydrolysis, ease of handling, cost of the material and titanium content are all well balanced and therefore, this ester has become commercially important.

Butyl titanate is a versatile compound and it is used in various industries. In heat resisting paints it is utilised usually with metallic aluminium and can resist temperatures upto 600°C. In addition, butyl titanate reduces water permeability and water adsorption of paint films and also enhances their heat resisting properties. Metallic driers can be replaced by butyl titanate.

Materials applied with silicone resins for having a heat resistant finish have to be heated upto 150°-250°C. before the resin is cured, but this is not possible in case, textile and leather are to be coated with this resin. A first coat of butyl titanate makes it possible to decrease the temperature and time of curing of the resin.

In view of the importance of butyl titanate in paint industry, systematic studies on butyl titanate have been undertaken.

Butyl titanate

The history of titanium esters demonstrates the very recent interest in them. The first real mention of such compounds was not until 1875, when Demarcay[3] investigated the reaction between titanium tetrachloride and ethyl alcohol. In 1892, Levy extended the range of hydroxyl compounds reacted with titanium tetrachloride, but it was not until 1936, that Jennings, Verdier and Way[4] assigned the correct formula to Demarcay's compound. In the meantime, Bischoff and Adkins[5] had prepared some of the true ortho-esters of titanium. Immediately prior to war, I.G. Farbenind[6] patented a novel method of preparation but little further work was published until the Australian Council for Scientific and Industrial Research started examining possible uses for the deposits of titanium ores in the Commonwealth. This appears to have stimulated interest in titanium esters. Since then there has subsequently been a continually increasing volume of literature concerning them.

Bishoff and Adkins[5] prepared the tetra-methyl, iso-propyl and normal butyl titanates for the first time in 1924. The solid ethyl ester prepared by Demarcay was shown by them to be a mixture of oxy-ethyl titanates. Demarcay[3] allowed titanium tetrachloride to react with absolute alcohol to give the substance $TiCl(OC_2H_5)_3 . HCl$. This was then treated with sodium ethoxide. The method is not good in that the tetrachloride reacts with the alcohol to give some ethyl chloride and water. All the alkyl titanates react instantly with water so that the latter hydrolyses the esters to a certain extent and hence oxy-esters are obtained. The true tetraethyl ester may be obtained in a very small yield from the mother liquor from which Demarcay crystallised oxy-esters. Direct interaction of an alcohol and titanium tetrachloride causes hydrolysis of only two chloride atoms (V).

$$TiCl_4 + 2ROH = TiCl_2(OR)_2 + 2HCl \qquad V$$

Using ethyl alcohol, the chloro-ester can be separated as a crystalline solid containing alcohol of crystallisation, $Ti(OC_2H_5)_2Cl.C_2H_5OH$. This was the compound isolated by Demarcay to which he ascribed the formula $TiCl(OC_2H_5)_3.HCl$. However, if the hydrochloric acid be removed as soon as possible, the remaining two chlorine atoms may be removed (VI

$$TiCl_2(OR)_2 + 2ROH = Ti(OR)_4 + 2HCl \qquad VI$$

Bishoff and Adkins[5] used sodium to remove hydrochloric acid (VII).

$$TiCl_4 + 4ROH + 4Na = Ti(OR)_4 + 4NaCl + 2H_2 \qquad VII$$

They dissolved sodium in the alcohol to get the sodium alkoxide and then reacted one molecular equivalent of titanium tetrachloride with four molecular equivalents of sodium alkoxide in alcoholic solution. The yields of esters are good when the concentration of reagents and time of reaction are carefully controlled. The metallic sodium method suffers from disadvantage of the expense and inconvenience and to a lesser extent from the increasing difficulty of its reaction with higher alcohols.

The most versatile method and the one used for commercial production was devised by Mellor[7] and Kiselev and Ermolaeva.[8] I.G. Farbenind[6] also adopted this method successfully. Titanium tetrachloride is allowed to react with alcohols or phenols in the presence of anhydrous ammonia to remove the hydrogen chloride as ammonium chloride (VIII).

$$TiCl_4 + 4ROH + 4NH_3 = Ti(OR)_4 + 4NH_4Cl \qquad VIII$$

This method thus consists of adding titanium tetrachloride to a large excess of alcohol or an inert solvent and alcohol mixture, passing the ammonia gas, filtering off the precipitated ammonium chloride and finally evaporating. The titanium ester remains as the residue in the reaction flask, whilst excess of alcohol and solvent are recovered and reused. The alcohol may first be saturated with ammonia and then the chloride added.

Another method of preparation of these esters is the alcoholysis of an ester of a lower alcohol with one of a

higher boiling point (IX).

$$Ti(OR)_4 + 4R'(OH) = Ti(OR')_4 + 4ROH \qquad IX$$

Equilibrium occurs on simple mixing. During subsequent evaporation the lower boiling alcohol is removed leaving the titanium ester of the higher boiling alcohol. The titanium ester remaining in this case or in the metallic sodium and ammonia methods need not be further purified. However, if this is required distillation is always carried out at only a few millimeter pressure to avoid decomposition.

Titanium tetrachloride

The main bottleneck in the manufacture of butyl titanate in India is the non-availability of titanium tetrachloride, which is the starting material for the preparation of the titanate. In India at present, Travancore Titanium Products, is the only factory producing anatase from ilmenite with an annual capacity of 1,800 tons. The proposed plant at Bombay will have a capacity of 4,500 tons per year. Titanium dioxide is the only compound at present manufactured and only anatase variety is produced. It is expected that the factory proposed to be started at Bombay will produce titanium tetrachloride in sufficient quantities and pave the way for the production of different titanium chemicals for use in various industries in India and also for export, earning valuable foreign exchange.

The principal source of titanium is ilmenite ($FeOTiO_2$). The name of the mineral is derived from Ilmen mountains in the Urals of Russia where it was first discovered. The other ore of titanium is rutile (TiO_2) which

is much less abundant. India is the largest producer of ilmenite. It occurs as beach sands on the Malabar Coromandal coasts. The estimated reserves are of the order of 20 million tons. Australia, Brazil, Canada, Norway, Soviet Union and United States are the other countries which are rich in titanium ores.

Bauxite sludge is another important source of titanium. Indian bauxites contain 6-8% titanium dioxide. The bauxite sludge after extraction of aluminium called the red mud, contains about 30% TiO_2. But in view of the cheap and ready availability of ilmenite a richer source of titanium, commercial exploitation of 'red mud' for the recovery of titanium chemicals has not yet been attempted.

Ilmenite mining is relatively simple. When found in sand deposits, it is collected by suction dredgers, pumped to conditioner barges and then to concentrating plants. In order to separate the mineral components effectively, the raw ore is first ground to a fineness of 20 mesh. A low intensity, wet magnetic method is next used to separate all extraneous materials from the ilmenite. The remaining ilmenite is then concentrated in hydraulic classifiers and tables. Further upgrading of the concentrate is affected by a high intensity dry magnetic separation.

Usually about 40% of the raw ore consists of iron oxide. To avoid contamination of titanium tetrachloride with iron chloride specifically when chlorination process is used for its production, it is necessary to upgrade the

ore by removal of iron. The upgrading is done by heating with 23° Be' hydrochloric acid in 1:2.5 ratio by weight at 100°-150°C under steam pressure in a digester when iron goes into solution as iron chloride.

Vigouroux and Arrivant[9] were the first to suggest removal of iron by the action of hydrochloric acid. Pamfilov and Shtandel[10] removed iron by boiling with 20% hydrochloric acid for 24 hours. Ilmenite and bauxite sludge have been upgraded by heating with sulphuric acid or hydrochloric acid or their mixture. Chlorination in presence of insufficient amount (7% on weight of ilmenite) of carbon results in preferential chlorination of iron. Kharkar and Patel[11] used this method for upgrading the titania content from 59 to 90 percent. Using batch fluidised reactor and carbon monoxide as reducing agent, Doraiswamy, Bijwat and Kunte[12] have reported conditions for preferential chlorination of iron.

The upgraded ore is briquetted with low ash coke or charcoal and chlorine is passed over it at 600°-800°C. Chlorination is done in two stages; at lower temperature ferric chloride is formed and volatilised and at next higher temperature titanium oxide reacts with chlorine and carbon to yield titanium tetrachloride, a colourless liquid boiling at 135°C.

Titanium tetrachloride was first prepared in 1825 from ferrotitanium. Other titanium-bearing materials used in the studies on the preparation of titanium tetrachloride

consist of rutile, ilmenite[11,13], slag[13,14] (68% TiO_2) and bauxite sludge. The chlorination of titanium monoxide proceeds at considerable rate even at 300°C[15] while chlorination of titanium dioxide commences above 800°C. Chlorination of rutile takes place at a higher temperature than that of anatase.[16] Titanium sesquioxide and titanium dioxide are preliminarily reduced to titanium monoxide to facilitate chlorination. Aluminium[17], titanium[15], lamp black, wood chips[18], wood charcoal[19,20], sugar charcoal[17], coal[11,13], anthracite[20], coke[20], lignite and carbon monoxide have been used as reducing agents. When carbon is used, titanium carbide is also formed at 200°C which is decomposed by chlorine easily at 200°C.

Various binders such as starch[21], thin tar[22], ferric chloride[11] have been suggested and addition of small amounts of alkali has been patented for obtaining pellets which do not crumble during chlorination.

For acceleration of the chlorination several catalysts e.g. MnO_2[10,11], CuO, PbO, $Ca_3(PO_4)_2$ and CeO[11] and chlorination in co-operation of N_2[16], O_2, H_2O, S_2Cl_2, H_2S and CCl_4[11] have been used.

Chlorination hasbeen carried out in silicon carbide tube furnace, silica reactor, magnesite lined electric smelting furnace and batch fluidisation reactor.[12] The briquettes are coked to develop a hard, tough structure and to eliminate volatile matter.

The exit gases are absorbed in lead absorption tower containing sodium carbonate solution,[22] or through solid

chlorides condenser consisting of water jacketed tube and a jacketed chamber of larger cross section to decrease the upward gas velocity and accomplish settling of the solids.[13]

Titanium tetrachloride is freed of organic impurities by refluxing the crude tetrachloride in presence of $AlCl_3.6H_2O$ plus H_2O catalyst.[23] The chlorine is removed by passing clean, dry air through the boiling titanium tetrachloride. Vanadium is best removed with clean copper after the chlorine treatment. Vegetable oils have also been used to remove vanadium. Processes have been patented in which (1) gaseous titanium tetrachloride is freed of chlorides of iron and aluminium by passing it through a vessel maintained below the dew point of titanium tetrachloride and equipped with an agitator so that the incoming gas is violently scrubbed with a slurry containing solid particles of $FeCl_2$, $FeCl_3$ and $AlCl_3$ suspended in liquid titanium tetrachloride and (2) using only one condensation tower and effecting condensation by recycling cold titanium tetrachloride in an amount 50-100 times greater than the amount furnished by the chlorination furnace.

The present investigation aims at a systematic study of the properties of butyl titanate. As butyl titanate is imported and not readily available, experiments were done on the preparation of butyl titanate. Since titanium tetrachloride which is the starting material for butyl titanate is also not being manufactured in India, this was prepared in the laboratory. As the aim was to obtain pure

titanium tetrachloride, indigenously available anatase titanium dioxide was used and contamination of impurities was avoided by using low ash petroleum coke as reducing agent. A study of physico-chemical properties of butyl titanate, which have a bearing on its applications, was made and is reported in this part.

M E T H O D S

Differential Thermal Analysis

Leeds and Northrup D.T.A. apparatus was used. It is automatic recording type and consists of furnace, heating controller and differential and sample temperature recording units and sample holder. The electrically heated furnace is of horizontal tube type of 4.5 cm. diameter and 20 cm. length and can hold two sample holders. The maximum operating temperature is limited to 1000°C. The heating control for the furnace consists of (a) continuous curve recording equipment with automatic reference junction compensator and automatic current standardizer, (b) electric control unit, (c) motor operated variable transformer and (d) control panel. This unit records the temperature of the furnace control thermocouple, placed near the core of the furnace, in a continuous curve and is capable of giving a fixed uniform rate of heating of 12.5°C per minute from room temperature to 1000°C automatically. It also provides controlled rate of cooling. The differential and sample temperature recording unit comprises of (a) speedomax recorder which gives continuous curve of

differential electromotive force and travels 2.5 cm. for each 150°C, (b) stabilized microvolt D.C. amplifier used in circuit to amplify the small differential electromotive force produced by noble metal differential thermocouple; its sensitivity can be varied to suit the material to be studied for measuring and recording the differential electromotive force and (c) the control panel for holding the recorder, D.C. amplifier and a transformer to reduce 230 volts to 115 volts.

The sample holder is made of recrystallised alumina fired to 1600°C. It is of Roberts and Grimshaw pattern and has two compartments each with the capacity to hold 0.4 g. of material. The thermocouple used is platinum-10% rhodium and platinum which can be used upto a temperature of 1600°C.

The sample is ground to pass 60 B.S. mesh kept in vacuum disiccator over sulphuric acid for ~3 days before it is subjected to D.T.A. The sample is weighed nearest to 1 mg., packed uniformly in one of the compartments of the sample holder and the other compartment is filled with a similar weight of inert material i.e., calcined alumina. Uniformity of packing is maintained by pressing the sample and the reference material with a small die. The heating block containing the sample holder is properly positioned in the furnace. The thermocouple wires are connected to the lead wires and are led into blind tubes dipped in water in a vacuum flask which acts as temperature equaliser and

prevents the development of spurious electromotive forces. No cold junction temperature correction is necessary as the recorders are equipped with automatic reference junction compensators. After the necessary thermocouple connections are made, the X-Y recorder, preamplifier, programme controlling recorder are switched on, the electromotive force of the dry cells of X unit and Y unit in X-Y recorder, and of the programme controlling recorder are standardised against the standard cell. The furnace main is then switched on and the programme control is started and the switch for the pen in the X-Y recorder is put on. Subsequently a continuous curve of differential electromotive force versus temperature of the sample is recorded.

X-ray Diffraction

X-ray diffraction patterns were obtained by means of a Raymax crystallographic unit equipped with Debye-Scherrer type Unicam powder camera of radius 9.5 cm. and nickel filtered CuK_{α} radiation. Samples were prepared from Titanium dioxide (200-300 B.S. mesh) obtained by heating the hydrolysate mixed with Canada balsam and rolled into a specimen in the form of a rod approximately 0.25 mm. in diameter which could be mounted in the powder camera. An exposure period of 3 hours was used, the tube current and voltage being 20 ma. and 32 kV respectively. The films were developed and fixed under identical conditions.

Ultraviolet Absorption Spectrum

Beckman Quartz Spectrophotometer model DU 1206 was used for determination of ultraviolet absorption spectrum. The spectrophotometer consists of lamp house, monochromator, battery compartment, cell compartment mounting block, cell compartment, phototube house and phototube load resister box. The source for ultraviolet light is a hydrogen lamp. Most of the optical compartments of the instrument are located in the monochromator. The slit plate containing the entrace and exit slits for the light beam is attached to the right end of the monochromator. The block attached to slit plate contains a three position filter slide and the diagonal slit entrance mirror which reflects the light through the entrance slit. In the phototube house are located a red sensitive and blue sensitive phototubes for detecting energy transmitted through the standard and the sample. It also contains a positioning mechanism for the phototubes and shutter assembly for controlling the passage of light to the phototubes. The photo load resister box serves as a back cover plate for the phototube house and as a housing for a 2000 megohm load resister. Light from the hydrogen lamp is focussed by condensing mirror and directed in a beam to diagonal slit entrance mirror. The entrance mirror deflects the light through the entrance slit and the monochromator to the collimating mirror. Light falling on the collimating mirror is rendered parallel and reflected to the quartz prism when it undergoes refraction. The back surface of

the prism is aluminised so that light refracted at the first surface is reflected back through the prism, undergoing further refraction as it emerges from the prism. The desired wavelength light is selected by rotating the wavelength selector which adjusts the position of the prism. The spectrum is directed back to collimating mirror which centres the chosen wavelength on the exit slit and sample. Light passing through the sample strikes the phototube causing a current gain. The current gain is amplified and registered on the nulmeter. The silica cells used are perfectly matched and are of 1 cm. optical path.

Infrared Absorption Spectrum

Beckman Infrared Spectrophotometer model IR-2 was used. The principal unit consists of a closed monochromator mounted in a metal housing to which are attached radiation source, cell compartments and other accessories. The radiation source is Nernst glower requiring 60 watts of power. The glower is self-starting and its radiation output is automatically held constant within 0.1 percent by photoelectric regulator. The monochromator uses a 60 mm. base fixed rock salt prism. The wavelength range of the instrument with rock salt prism is 1 to 15 microns. Vapour tight cell with light path length of 0.1 mm. consists of stainless steel body holding two plain rock salt windows separated by a lead spacer gasket. Permanent record of the spectrum is automatically obtained on a light pen speed steep chart.

Preparation of Spectrophotometric Grade Chemicals

S.P. Butyl alcohol: Spectrophotometric grade butyl alcohol was prepared following the method recommended by Jones and Christian.[24] Chemically pure butyl alcohol was allowed to stand over freshly ignited calcium oxide for 24 hours. It was refluxed twice over 50 g. freshly ignited calcium oxide per litre of the alcohol for 4 hours. The alcohol was then decanted from the lime, kept over magnesium ribbon for a week and distilled over sulphanilic acid. The alcohol showed complete transmission at 252 millimicrons.

S.P. ethyl alcohol: As reported by Leighton and his co-workers[25], 95 percent ethyl alcohol was distilled over water-bath with 30 ml. of 12 N sulphuric acid per litre of the alcohol and the distillate was heated under reflux with 20 g. of potassium hydroxide and 10 g. of silver nitrate (dissolved in 3-4 ml. of distilled water) and distilled. The distillate was allowed to stand over amalgamated aluminium for one week. It was filtered and distilled again which gave complete transmission at 251 millimicrons.

S.P. Carbon tetrachloride: Carbon disulphide which is the most objectionable impurity in this solvent, is removed by boiling with dilute alkali.[26] Carbon tetrachloride was shaken with 1.5 times the amount of potassium hydroxide dissolved in equal volume of water and 100 ml. ethyl alcohol for 30 minutes at 50-60°C. The tetrachloride thus separated was then washed with distilled water several times, dried

over anhydrous calcium chloride for a week and thrice distilled. The tetrachloride showed complete transmission at 295 millimicrons in the ultraviolet region.

S.P. methyl alcohol: S.P. methyl alcohol was used as supplied by GMBH and Co., Munchen.

Chemical Analysis

Titanium dioxide: Titanium dioxide was analysed for iron and titanium as per the method recommended by Gooch.[27] About 1 g. titanium dioxide was taken in a silica crucible and fused with 12.5 g. potassium pyrosulphate for 3 hours. The melt containing titanium sulphate was dissolved in water, washed firstly with water acidified with sulphuric acid and finally with water. The residue was fused with about 1.3 g. potassium pyrosulphate, the melt leached with acidified water, kept overnight, filtered and washed. The insoluble residue was weighed. To the filterate 3 g. tartaric acid was added, hydrogen sulphide gas passed in it and ammonium hydroxide added to have a slight alkalinity. Hydrogen sulphide was passed again till complete precipitation of iron as iron sulphide.

20 ml. A.R. sulphuric acid was added to the clear solution after separation of iron and evaporated in a 500 ml. Kjeldahl flask till the tartaric acid in the solution charred. 10 ml. fuming nitric acid was added to the cooled residue dropwise when white fumes of sulphur trioxide were given off. The solution was cooled and ammonia added to precipitate titanium as titanium hydroxide. The precipitate was washed with ammonium nitrate solution followed

by water, ignited and weighed as titanium dioxide.

Petroleum coke: Method recommended by Stockdale and Dexter[28] was adopted for the analysis of petroleum coke. Volatile matter and ash contents were estimated and fixed carbon was determined by difference. About 1 g. of finely powdered (-100 B.S. mesh) petroleum coke was heated in a silica crucible covered with lid in a muffle furnace at 925°C for 7 minutes. The crucible was removed from the furnace, cooled to room temperature and the loss in weight determined gave volatile matter and moisture in the coke sample. The lid of the crucible was removed and the crucible was heated in a muffle furnace to constant weight giving ash content of the coke.

Titanium tetrachloride: $TiCl_4$ collected in the receiver was cooled to -30°C in an ice-magnesium chloride bath. A.R. hydrochloric acid taken in a separate flask was cooled to same temperature. Equal volumes of the two liquids were mixed. 2 ml. of the mixture were taken in an Erlenmeyer flask (25) ml.) and diluted with distilled water. Excess amount of ammonia was added in small amounts with continuous stirring. The hydrolysate was filtered, washed free of chloride, dried and ignited to a constant weight. From the weight of titanium dioxide thus obtained the titanium chloride content in the liquid was calculated.

Titanium Tetrachloride Unit

The arrangement of the apparatus for the preparation of titanium tetrachloride is shown in Fig. 1. The

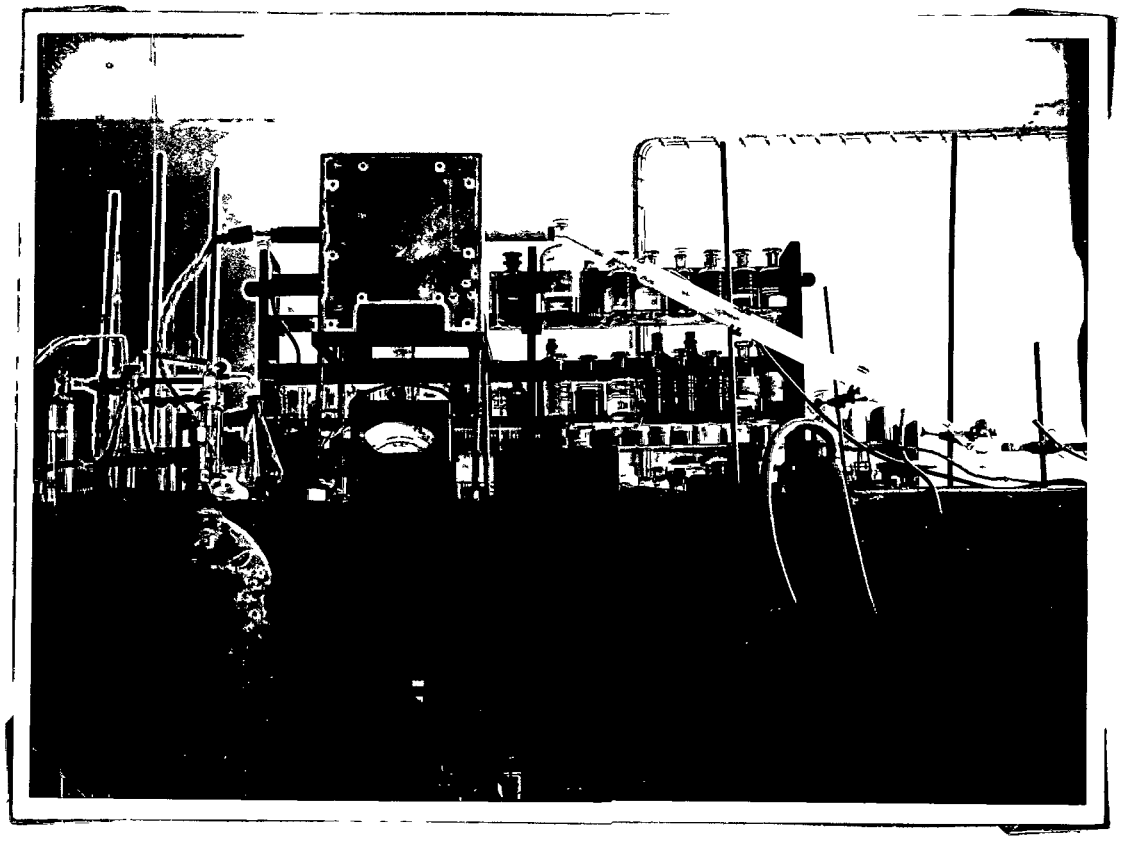


Fig. 1. Titanium tetrachloride unit.

apparatus consists of an electric tube furnace provided with sunvic energy regulator for controlling the temperature. A vitreosil silica tube 2.5 cm. dia. x 55 cm. length in which chlorination reaction is carried out is placed in the furnace. One end of the tube is connected to the chlorine gas cylinder through a monometer and bubblers filled with concentrated sulphuric acid. The other end of the tube is attached through B_{14} ground glass joint to a condenser, maintained at 5°C by iced water circulated by a pump. At the end of the condenser a receiver is provided which is connected to bubbler containing hydrochloric acid for removing excess gases provided with exhaust tube open to atmosphere. The temperature is measured by means of chromel-alumel thermocouple inserted in the silica tube in the middle of the reaction zone. The thermocouple is closed in a silica sheath to avoid contact with chlorine and other gases. The reaction temperature is measured on an indicator. The indicator was calibrated prior to its use with a standard temperature indicator.

Butyl Titanate Unit

The unit for the preparation of butyl titanate consists of a five-necked round bottom pyrex flask of 2 litre capacity placed in an ice-salt bath kept at below 0°C. The flask is fitted with a mechanical glass stirrer with a mercury seal, a thermometer ranging -10° to 110°C, a dropping funnel of 250 ml. capacity, a bubbling tube for

passing ammonia and an outlet for exhaust gases.

Preparation of Titanium Tetrachloride

Petroleum coke received from Assam Oil Co. and anatase titanium dioxide supplied by Travancore Titanium Products were used in the preparation of titanium tetrachloride. Mixtures of coke and titanium dioxide in different proportions were prepared in 100 g. batches. Coke was powdered to pass 100 B.S. mesh in a pot mill and titanium dioxide was used as supplied (-300 B.S. mesh). The coke and titanium dioxide were homogeneously mixed in a pot mill for 4 hours. Granules (1 mm. dia.) of coke-titanium dioxide mixtures in five different proportions were prepared in a granulator using water as a binder. The granules were dried at 110°C for 6 hours before their use.

Experiments were done at 750°C using coke-titanium dioxide mixture in different proportions with a view to determine optimum proportion of coke required. Using the optimum coke-titanium dioxide proportion (1:3), experiments were then done at six different temperatures in the range of 500° - 900°C.

To remove volatile matter and moisture from the coke, the granules were heated at 900°C in a tube furnace in a vitreosil silica tube closed at one end and attached to a condenser on the other end till fumes ceased to come out from the tube. Usually 2 hours were required for completion of this operation, after which the open end of the tube was closed and cooled to room temperature.

The granules were removed from the tube and weighed to check up whether the loss in weight corresponded to the volatile matter and moisture in the coke. It was observed that in all the cases complete removal of the volatile matter and moisture took place when the granules were heated at 900°C for 2 hours.

The devolatilised granules were taken in another vitreosil silica tube and placed in the furnace and heated to the desired temperature at a constant rate of 16°C per minute. Chlorine was passed through the granules when the temperature was about 200°C and continued for 3 hours at the desired temperature. Since the reaction was observed to be completed in about 3 hours, all the experiments were carried out keeping reaction time constant (3 hours) and varying proportion of reactants and temperature. The extent of conversion of titanium dioxide to titanium tetrachloride was determined by weighing titanium tetrachloride collected in the receiver. After the end of the experiment when the silica tube attained room temperature, it was opened and its contents examined.

Analysis of Product Gases

Product gases were analysed for the amount of carbon dioxide and carbon monoxide after every one hour. 330 ml. of gas was collected in each case by displacement of water. The jars containing the flue gases were inverted over a saturated solution of potassium hydroxide. As the amount of chlorine in the gases was negligible, the rise of water level in the jar was taken as the amount of carbon

dioxide. Carbon monoxide was calculated by difference.

Preparation of Butyl Titanate

Butyl titanate was prepared using titanium tetrachloride prepared from titanium dioxide as described above. Titanium tetrachloride was 98.6% pure and free of impurities excepting chlorine. Butyl alcohol was distilled at 116° - 117°C before use. 105 g. of titanium tetrachloride were taken in a dropping funnel and added slowly with continuous stirring. Heat was evolved in the reaction and rate of addition of titanium tetrachloride was never exceeded 0°C. Titanium tetrachloride was added in about 1.5 hours. Ammonia gas dried by passing through the drying towers containing soda lime was bubbled through the reaction mixture for 3 hours keeping the temperature of the contents in the flask in the range of -8° to 0°C. The precipitated ammonium chloride was filtered off through a G3 sintered glass Buchner funnel. The filterate thus obtained was a solution of tetra n-butyl titanate in butyl alcohol. The titanate was separated from butyl alcohol by distillation. It was further distilled thrice under vacuum in an atmosphere of carbon dioxide at a residual pressure of 3 mm. of mercury at 174°C.

RESULTS AND DISCUSSION

Factors affecting the yield of titanium tetrachloride

Analysis of titanium dioxide and petroleum coke used is shown in Table 2. Table 3 and Fig. 2 show the

yield of titanium tetrachloride at 750°C when the proportion of coke in the reaction mixture is varied.

Table 2

Analysis of Titanium dioxide and Petroleum Coke

Titanium dioxide	%	Petroleum Coke	%
TiO_2	99.56	Volatile matter	12.01
Fe_2O_3	Nil	Ash	0.50
Insoluble matter	0.38	Coke (by difference)	87.49

Table 3

Effect of amount of coke on yield of titanium tetrachloride

Petroleum coke % by wt. of mixture	Temperature °C	Yield %
15	750	54.8
20	750	65.2
25	750	97.2
33	750	95.2
50	750	95.4

Table 4 and Fig. 3 give the results of experiments done to determine the effect of temperature using 25 percent coke which gives complete conversion and Table 5 presents the analysis of product gases.

With 15 percent coke in the mixture the yield of titanium tetrachloride is 54.8 percent. The amount of titanium tetrachloride formed increases with the increase

in the proportion of coke in the coke-titanium dioxide mixture. Complete conversion to titanium tetrachloride is obtained using the coke to titanium dioxide in the mixture in 1:3 proportion. With higher proportion of coke also the conversion to titanium tetrachloride is complete.

Table 4

Effect of temperature on yield of titanium tetrachloride

Petroleum coke % by wt. of mixture	Temperature °C	Yield %
25	500	19.1
25	550	90.1
25	600	95.3
25	750	97.2
25	800	97.0
25	900	97.2

Table 5

Analysis of product gases on chlorination of titanium dioxide and petroleum coke mixture (3:1) by weight.

Temperature °C	Carbon dioxide % by volume
600	93.1
690	33.3
800	27.3
915	16.6

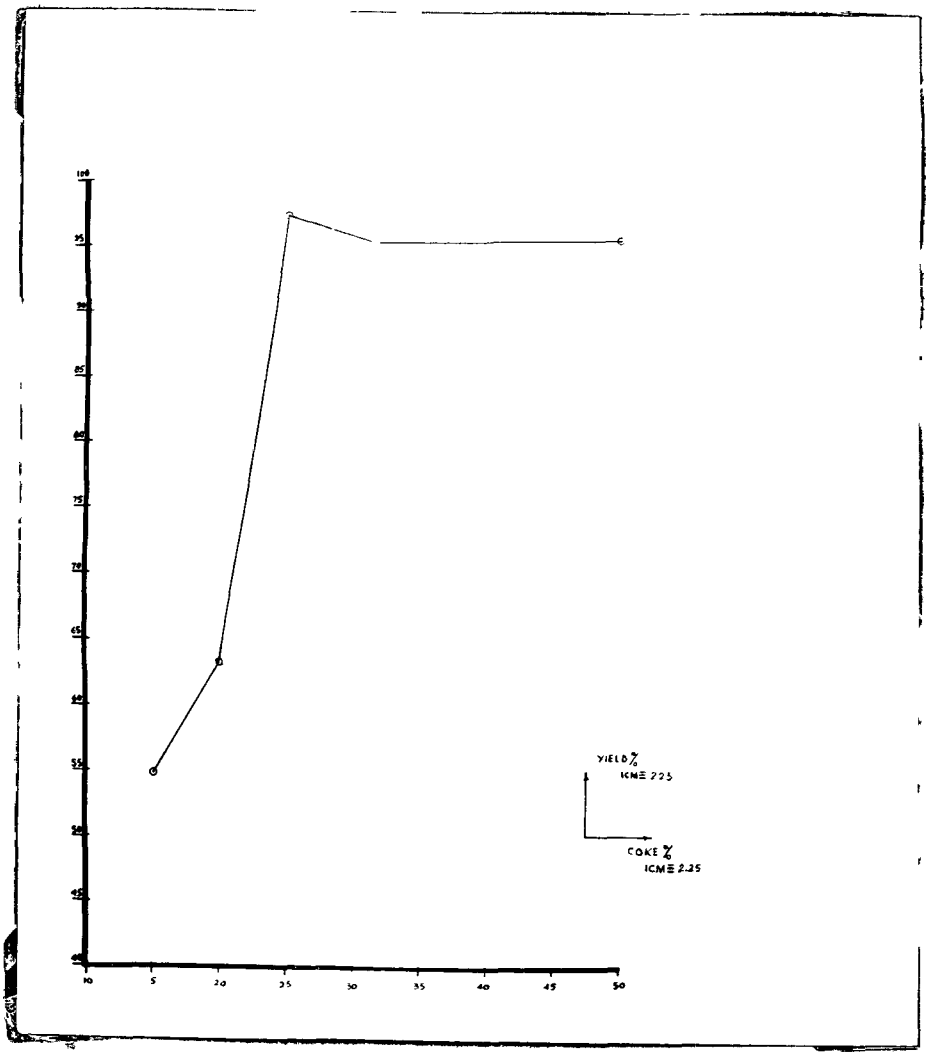


Fig. 2. Relationship between percentage of coke and yield of titanium tetrachloride

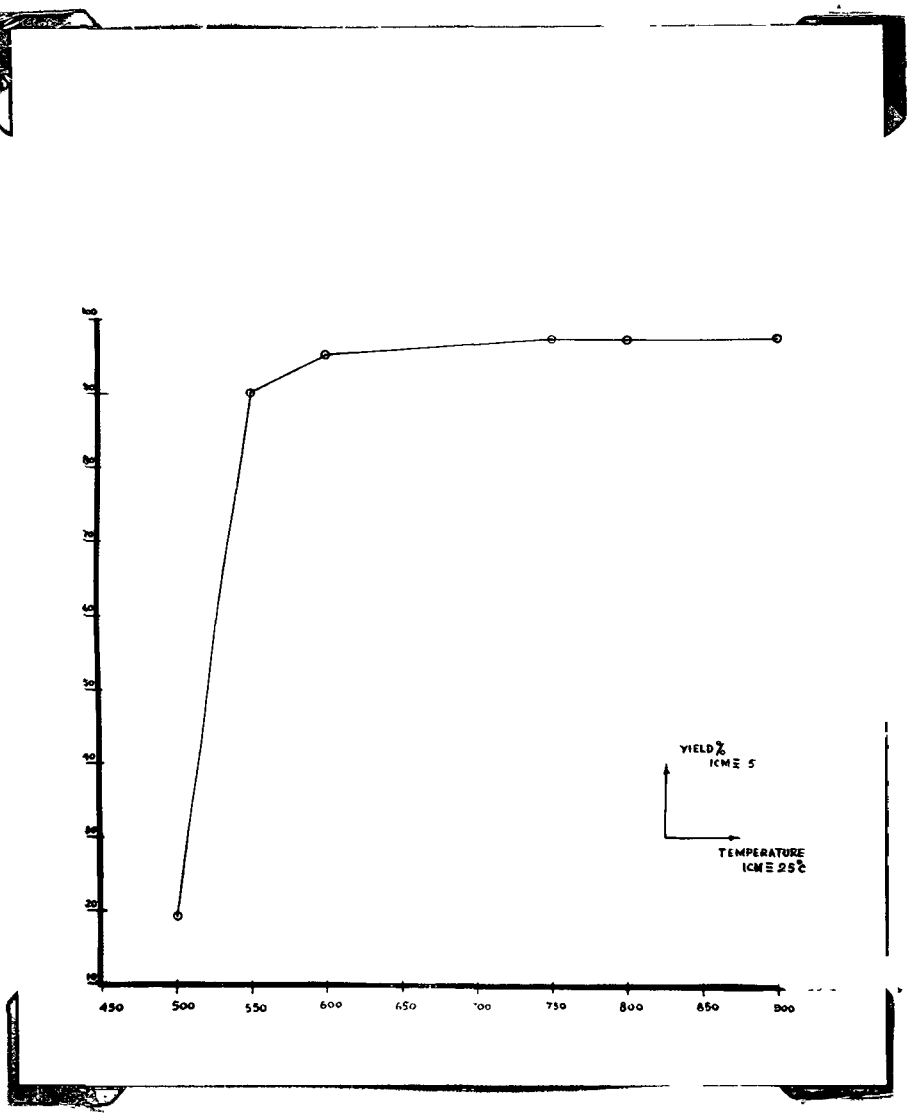


Fig. 3. Relationship between temperature of reaction and yield of titanium tetrachloride.

The residue left over in the reactor shows absence of titanium dioxide showing complete conversion of the dioxide to tetrachloride when percentage of coke in the mixture is 25 or more. This residue, however, shows presence of unreacted coke. About 12 percent of coke is found to remain unreacted when the ratio of coke to titanium dioxide is 1:3 indicating that 75 g. TiO_2 requires 22 g. coke and not 25 g. coke for completion of the reaction. In other words, requirement of coke is 29.33 percent on the weight of titanium dioxide. Since the coke used contains 87.5 percent fixed carbon, the actual amount of carbon taking part in the reaction on weight of titanium dioxide is 25.66 percent. Theoretical yield of 100 percent is not obtained due to incomplete condensation of titanium tetrachloride vapours. In fact presence of titanium tetrachloride is detected in the bubbler containing hydrochloric acid due to absorption of uncondensed titanium tetrachloride, resulting in the observed yield of 95-97 percent. The reaction between chlorine and titanium dioxide starts around 300°C as indicated by the appearance of white fumes from the reaction tube when temperature of 300°C is attained. It will be seen from Table 4 that at 500°C the conversion is about 20 percent when the temperature is increased from 500° to 550°C, the yield is increased from 19 to 90 percent. At 600°C, 800°C and 900°C the yields are 95, 97 and 97 percent respectively. This shows that most of the reaction takes place only in the region of 550°-600°C.

Mechanism of chlorination of titanium dioxide

The previous workers[10,15,20] have suggested that chlorination of titanium dioxide in presence of carbon takes place accompanied by formation of CO_2 upto 600°C and of CO above this temperature (XI, XII), while in the absence of carbon it proceeds with the formation of equimolar amounts of titanium tetrachloride and titanium dioxide (X). In the present experiments the reaction is taking place at lower temperature, 600°C, primarily with the formation of CO_2 according to (XI), but is vitiated by the side reaction according to (XII) at higher temperature (Table 5).

$$2TiO + 2Cl_2 = TiCl_4 + TiO_2 \qquad X$$

$$2TiO_2 + 2Cl_2 + C = 2TiCl_4 + CO_2 \qquad XI$$

$$TiO_2 + 2Cl_2 + 2C = TiCl_4 + 2CO \qquad XII$$

The requirement of carbon is therefore slightly higher than that for the reaction (XI). The theoretical requirements for reactions (XI) and (XII) are 15 and 30 percent respectively, whereas the carbon utilised in the reaction at 750°C using 1:3 proportion of coke and TiO_2 in the reaction mixture is 25.66 percent.

Preparation of butyl titanate

The interaction of titanium tetrachloride and butyl alcohol causes hydrolysis of only two chlorine atoms (XIII). However, if the hydrochloric acid is removed as soon as it is formed further reaction takes place with the removal of the remaining two chlorine atoms (XV). In this

method hydrochloric acid formed is removed as ammonium chloride formed by passing ammonia gas into the reaction mixture (XIV). The ammonium chloride is insoluble in the reaction mixture and is filtered off. The filtrate consists of butyl alcohol and butyl titanate from which butyl alcohol is separated by distillation and reused. The overall reaction may be represented by equation (XVI). Butyl titanate was analysed, titanium content was 13.98 percent as against theoretical value of 14.10 percent, showing that it was of 99.2 percent purity. 127 *g.* of pure butyl titanate was prepared for use in its physico-chemical properties.

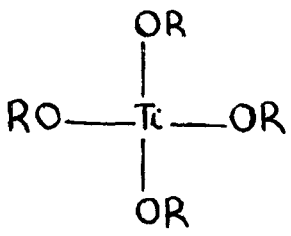
$$TiCl_4 + 2C_4H_9OH = TiCl_2(OC_4H_9)_2 + 2HCl \qquad XIII$$

$$HCl + NH_3 = NH_4Cl \qquad XIV$$

$$TiCl_2(OC_4H_9)_2 + 2C_4H_9OH = Ti(OC_4H_9)_4 + 2HCl \qquad XV$$

$$TiCl_4 + 4C_4H_9OH + 4NH_3 = Ti(OC_4H_9)_4 + 4NH_4Cl \qquad XVI$$

The yield of butyl titanate on the weight of titanium tetrachloride taken was 67.5 percent as against 49.7 percent reported (Table 1). The structural formula of tetra n-butyl titanate is shown in Fig. 4.



where R = C_4H_9

Fig. 4. Structural formula of tetra n-butyl titanate

Differential Thermal and X-ray Analysis of Hydrolysate of butyl titanate

Titanium dioxide exists in three forms anatase, rutile and brookite which are different in crystalline structure. Large volume of information is available on the preparation of anatase and rutile. The starting materials for the preparation of these two forms of titanium dioxide are titanium sulphate and titanium tetrachloride. The hydrolysate from titanium sulphate invariably gives anatase on calcination, which is converted to rutile on further heating at higher temperature. On the other hand, titanium tetrachloride hydrolysate on calcination yields rutile at lower temperature.

The transformation of the hydrolysate to various forms of titanium dioxide has been usually followed by x-ray diffraction, electron microscope, potentiometric titration and polarographic methods, since simple methods like determination of pH, refractive index and density have not been able to yield any accurate results. In recent years, differential thermal analysis has been adopted for following the various changes taking place during heating the hydrolysate and the method has been found to be very sensitive and convenient. The technique although not very recent has been used only by a few workers for this purpose and hardly about half a dozen references are available.

Sullivan and Cole[29] studied the changes taking place in the hydrous titanium dioxide prepared by the

hydrolysis of titanium sulphate by differential thermal analysis and observed two endothermic peaks at about 150°C due to loss of water and the other at 650°C due partly to the evolution of sulphur trioxide. A small exothermic peak at 900°C due to anatase-rutile transformation is observed. Recently, Jere and Patel[30] carried out differential thermal analysis coupled with x-ray diffraction and infrared spectrum studies on titanyl hydroxide precipitated from titanium tetrachloride. A shallow endothermic peak around 65°C is observed in the fresh sample which is due to the loss of loosely held water. The endothermic peak at 160°C is due to loss of water of constitution. The peak at 160°C is followed by an exothermic peak which is associated with the conversion of amorphous dioxide into crystalline anatase form of titanium dioxide. Another shallow exothermic peak appears at 600°C and extends well beyond 700°C, corresponding to the conversion of anatase into rutile.

The data on thermal decomposition of the hydrolysate of butyl titanate is meagre and differential thermal analysis and x-ray studies have not been reported. The results of the studies described below show that the hydrolysate of butyl titanate behaves essentially like that from titanium tetrachloride.

Butyl titanate (75 g.) was taken in a 250 ml. flask. Water was added drop by drop from a burette with continuous stirring till no further white precipitate of titanium hydroxide was formed. Titanium hydroxide was separated

by filteration and washed free of butyl alcohol till no blue colour developed with nitrochloric acid. It was dried under vacuum over concentrated sulphuric acid, for 72 hours and subjected to differential thermal analysis.

0.24 g. of the hydrolysate was taken in one compartment of the sample holder, the other compartment being filled with calcined alumina (0.4 g.). The hydrolysate and alumina were packed under same conditions and to same volume. The rate of heating was maintained at 12.5°C per minute and heating continued for about 90 minutes. The thermogram obtained is reproduced in Fig. 5. The thermogram exhibits endothermic peaks at 128°, 240° and 450°C and exothermic peaks at 315° and 600°C.

The endothermic peak at 128°C is due to the decomposition of titanyl hydroxide. The product still contains about 4.5 percent of water which it loses in stages at 240°C (3 percent) 315°C (0.9 percent) and 415°C (1.6 percent) accompanied by the transformation of amorphous titanium dioxide to crystalline anatase. The exothermic peak at 315°C due to the conversion of the amorphous dioxide into the crystalline anatase is preceded by an endothermic peak at 240°C (curve 1) which corresponds to the removal of the strongly held water (3 percent) and consequent rearrangement of the molecules in the dioxide structure. An endothermic peak is again observed at 450°C showing further loss of water of constitution. An exothermic peak appears at 600°C. This peak corresponds to the

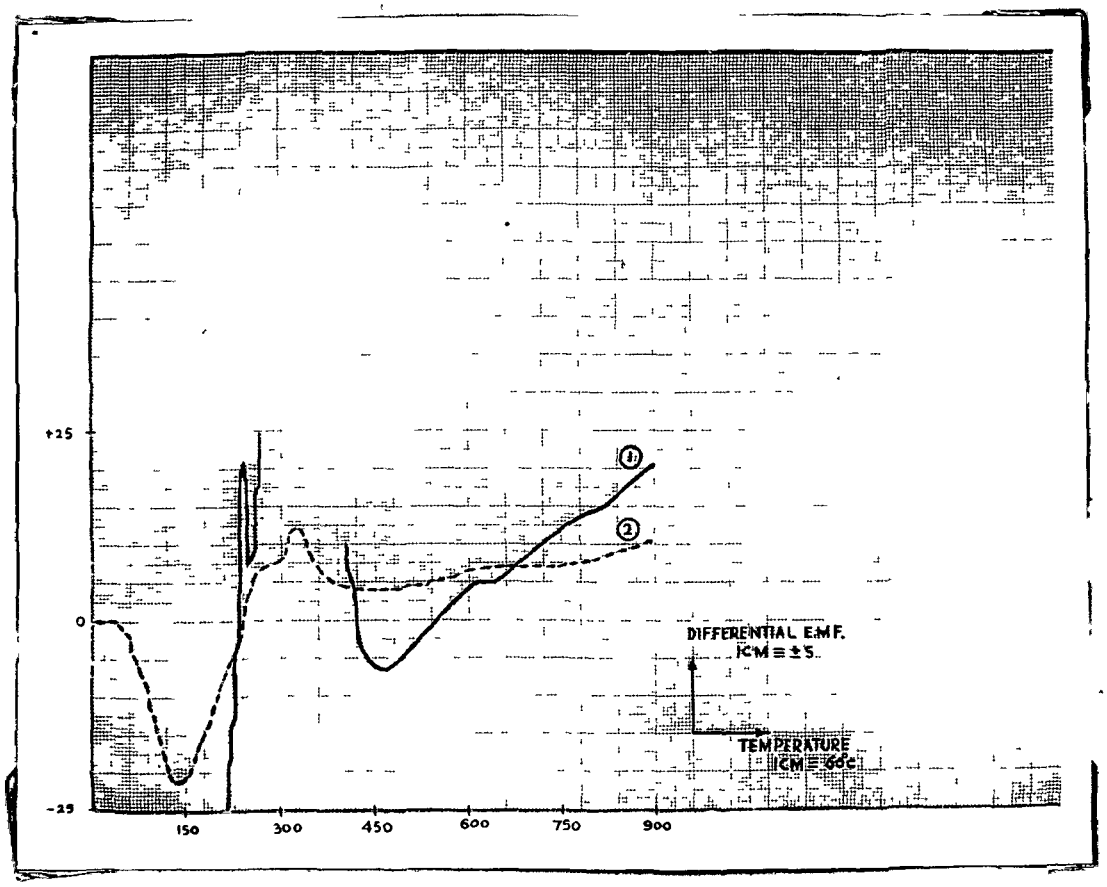


Fig. 5. Thermogram of hydrolysate of tetra n-butyl titanate (1) S.N. 10 & (2) S.N. 4.

beginning of the conversion of anatase into rutile.

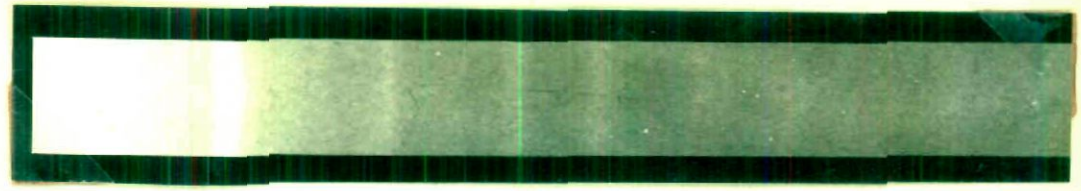
X-ray diffraction patterns of titanium dioxide obtained by heating the hydrolysate of butyl titanate at 128°, 240°, 315° and 450°C were taken (Fig. 6). In all cases the following d values (interplanar spacing) due to anatase were observed: 3.50 Å, 2.36 Å, 1.88 Å, 1.67 Å and 1.47 Å. The pattern of titanium dioxide obtained at higher temperature showed sharp diffraction lines indicating that it is better crystallised on removal of the last traces of water and consequent rearrangement of atoms and also as on heating the crystallite sizes of titanium dioxide are increased.

Ultraviolet absorption spectrum

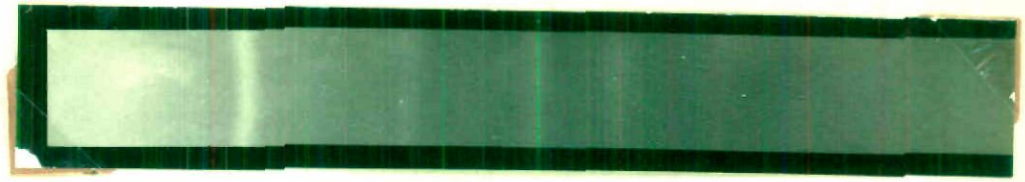
Although considerable interest has been shown in the preparation of butyl titanate and in its applications, a systematic study of its physico-chemical properties which will help in understanding its behaviour in paints and other applications has so far not been made. Ultraviolet absorption spectrum which has not been reported, has, therefore, been investigated.

Butyl titanate was dissolved in butyl alcohol (or ethyl alcohol) and made upto mark in a 250 ml. measuring flask. The requisite volume of this solution was diluted to obtain the final solutions e.g. 1.265×10^{-4} M in butyl alcohol and 1.213×10^{-4} M in ethyl alcohol. Also a solution of linseed oil in butyl alcohol (0.0172 g. per litre) and a solution of mixture of linseed oil and

(a)



(b)



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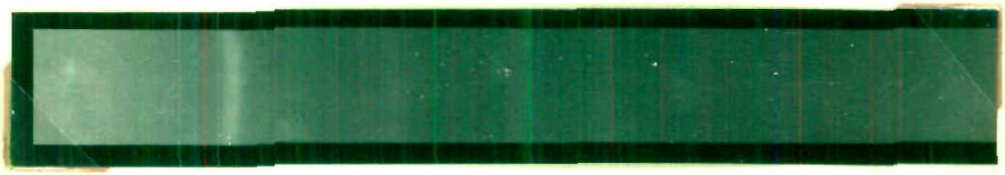

(d)

Fig. 6. X-ray diffraction patterns of hydrolysate of tetra n-butyl titanate heated to (a) 128°C, (b) 240°C, (c) 315°C & (d) 450°C.

butyl titanate in the alcohol containing 0.0172 g. of the oil and 0.0032 g. of butyl titanate per litre of solution were prepared.

Table 6

Absorbance of butyl titanate solutions in butyl and ethyl alcohols

Butyl alcohol solution		Ethyl alcohol solution	
Wavelength in millimicrons	Absorbance	Wavelength in millimicrons	Absorbance
220	0.26	220	0.90
222	0.44	222	0.93
225	0.66	224	0.94
228	1.00	226	0.95
230	1.12	228	0.955
232	1.17	230	0.955
234	1.19	232	0.96
236	1.195	233	0.96
237	1.20	234	0.9625
238	1.200	235	0.9625
239	1.1975	236	0.97
240	1.1975	237	0.97
242	1.17	238	0.96
245	1.12	240	0.955
250	1.00	245	0.90
255	0.90	250	0.84
260	0.78	255	0.785
265	0.67	260	0.74
270	0.56	265	0.695

(Table 6 contd.)

Butyl alcohol solution		Ethyl alcohol solution	
Wavelength in millimicrons	Absorbance	Wavelength in millimicrons	Absorbance
275	0.47	270	0.635
280	0.375	275	0.575
285	0.30	280	0.51
290	0.236	285	0.43
295	0.17	290	0.34
300	0.128	295	0.295
305	0.10	300	0.24
315	0.04	310	0.1375
320	0.012	320	0.065

Table 7

Relationship between absorbance and concentration of butyl titanate in butyl alcohol.

Concentration of butyl titanate in g./litre	Absorbance at 237 millimicrons
0.030100	0.8175
0.020060	0.54
0.015050	0.405
0.012040	0.3275
0.010030	0.27
0.008574	0.2325
0.007740	0.22
0.007225	0.205

In Table 6 are presented the values for absorbance of solutions of butyl titanate in butyl alcohol and ethyl alcohol. The absorption spectra from 220 to 320 millimicrons is also shown in Fig. 7.

Butyl titanate exhibits strong absorption band in the region 240 millimicrons. The absorbance at 220 millimicrons for the 0.0001205 M solution in butyl alcohol is 0.26 while the absorbance at the same wavelength for the 0.0001213 M solution in ethyl alcohol is considerably higher namely, 0.9. The absorbance value increases from 0.26 at 220 millimicrons to 1.2 at 237 millimicrons for solution in butyl alcohol whereas for solution in ethyl alcohol the increase is only from 0.9 to 0.97. The absorption band in butyl alcohol is sharp, the maximum absorption being at 237-38 millimicrons. The absorption band is broad for ethyl alcohol solution, the peak value being 236-237 millimicrons. It will be seen that although peak occurs at same wavelength the absorbance at the peak is lower in ethyl alcohol than in butyl alcohol. The absorbance value decreases and from 255 millimicrons onward the nature of the curve for the solutions in the two alcohols is same, the absorbance values for butyl alcohol being slightly lower than the values for ethyl alcohol solution at the corresponding wavelengths.

The relationship between concentrations of butyl titanate in butyl alcohol and its absorbance at 237 millimicrons was determined using eight different concentrations

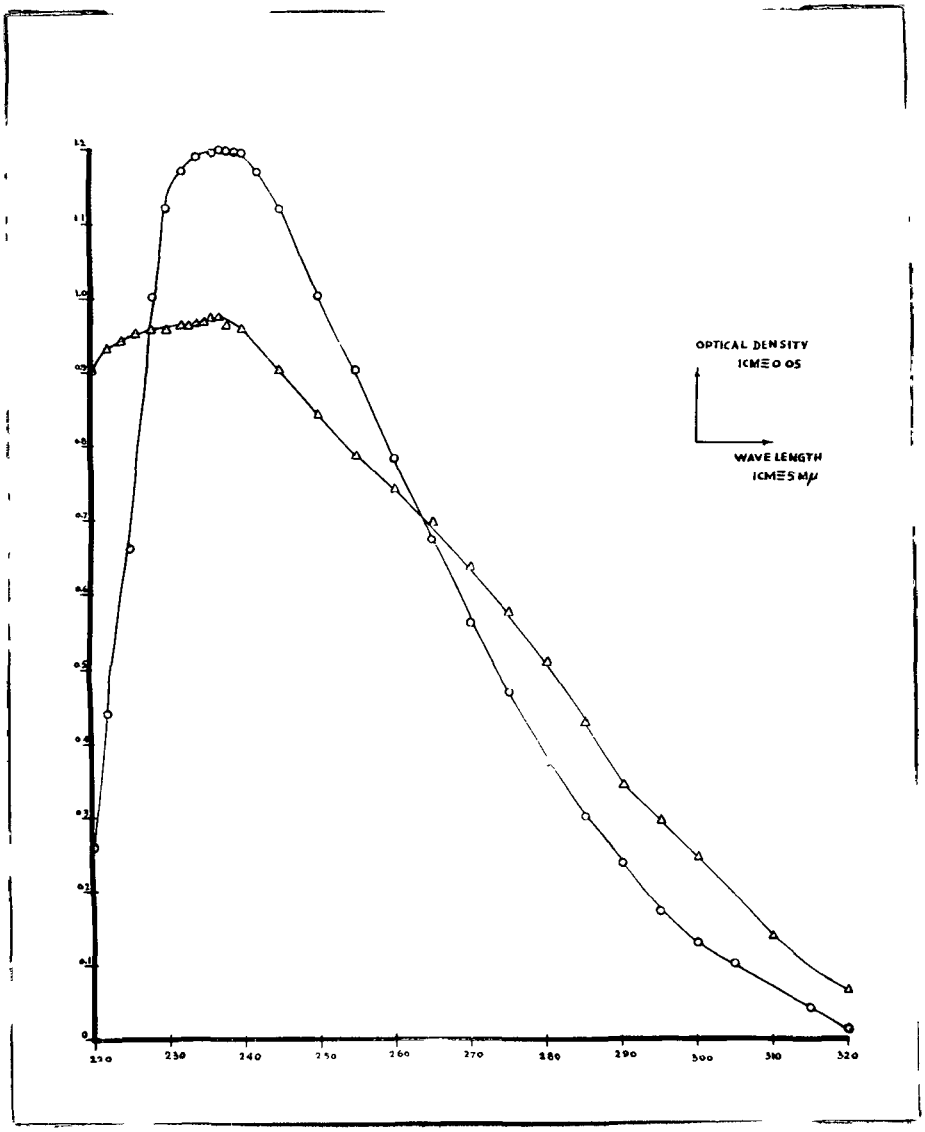

Fig. 7. Ultraviolet absorption spectrum of tetra n-butyl titanate in ⊙-n-butyl alcohol & △ -ethyl alcohol.

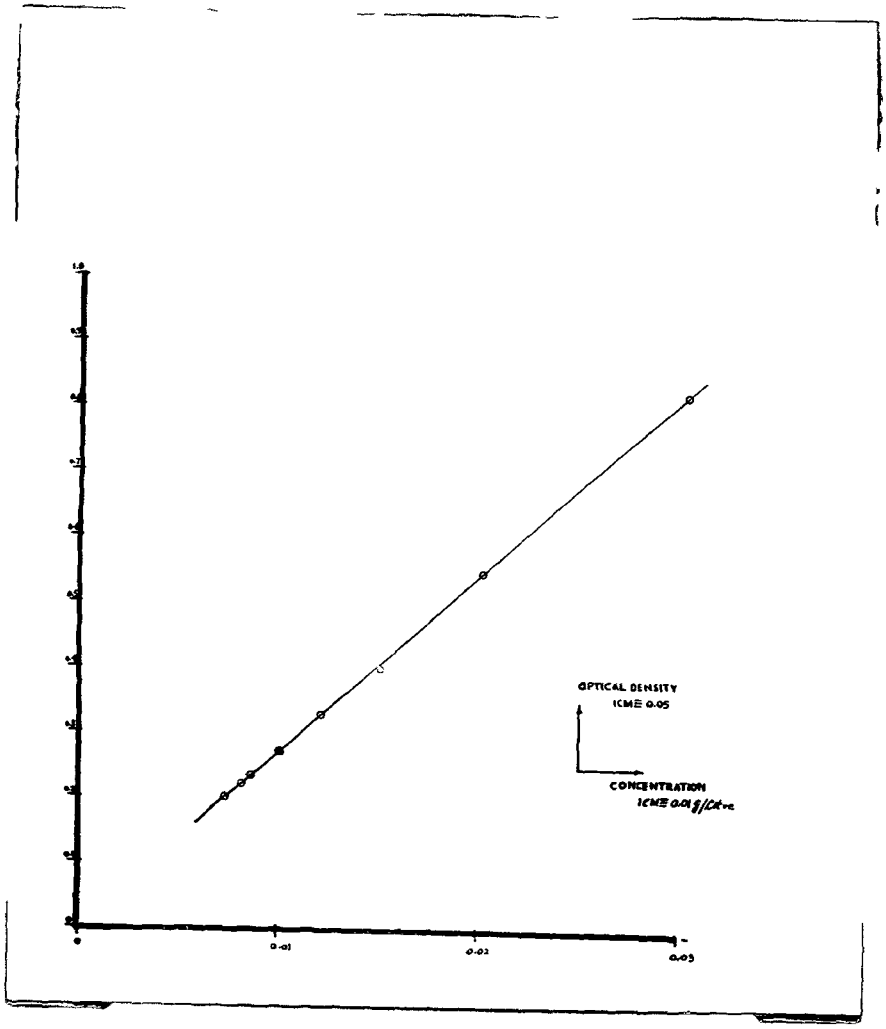

Fig. 8. Relationship between optical density and concentration of tetra n-butyl titanate in n-butyl alcohol.

from 0.007 to 0.03 g. per litre of butyl titanate in butyl alcohol. The optical densities at different concentrations are given in Table 7 and graphically shown in Fig. 8. The plot of optical density against concentration gives a perfect straight line. The linear relationship between optical density and concentration shows that butyl titanate obeys Beer's law.

The molecular extinction coefficients were calculated for butyl titanate in butyl alcohol at 237 millimicrons using the following formula:

$$K = \frac{d}{M \times l}$$

where K = molecular extinction coefficient
d = absorbance
M = molar concentration
l = length of optical path

The molecular extinction coefficients are 9300 in butyl alcohol and 8000 in ethyl alcohol.

The fact that butyl titanate obeys Beer's law suggests that spectrophotometric method may form a basis for itsaccurate determination. As most important application of butyl titanate is in paints where it is invariably used together with some drying oil like linseed oil, measurements of absorbance of butyl titanate and linseed oil mixture from 231 to 242 millimicrons were made and compared with those of linseed oil. The measurements were made in butyl alcohol solutions keeping the concentration of butyl titanate in both the cases constant. The

The results are given in Table 8.

Table 8

Absorbance of butyl titanate in butyl alcohol in presence of linseed oil.

Wavelength in milli-microns	Absorbance of linseed oil a_1	Absorbance of linseed oil + butyl titanate a_2	Difference $a_2 - a_1$
231	0.725	0.79	0.065
232	0.72	0.79	0.07
233	0.71	0.79	0.08
234	0.705	0.79	0.085
235	0.70	0.79	0.09
236	0.69	0.79	0.10
237	0.68	0.78	0.10
238	0.66	0.78	0.12
239	0.65	0.78	0.13
240	0.63	0.78	0.15
241	0.61	0.765	0.155
242	0.58	0.75	0.17

Attempt was made to correlate the absorbance at 237 millimicrons due to butyl titanate in linseed oil with the same of butyl titanate. The value for optical density observed for the solution in linseed oil is 0.1 for 0.0032 g. per litre concentration of butyl titanate. This is comparable to the value of 0.09 calculated from Table 7 for the solution of similar concentration of butyl titanate in butyl alcohol. However, this method will not

have general application as the concentrations of butyl titanate used ordinarily are very low and also as the spectrum of linseed oil masks the effect due to butyl titanate.

Infrared absorption spectrum

Butyl titanate is soluble in butyl alcohol, carbon tetrachloride, chloroform and normal hexane. The conventional technique of determining infrared absorption spectrum in solution could not, however, be employed because (1) butyl alcohol is not suitable as it masks the peaks of butyl titanate and (2) butyl titanate is easily hydrolysed in the presence of traces of moisture in other solvents. Therefore, infrared studies were carried out using butyl titanate liquid. In view of the fact that butyl titanate readily hydrolyses, it is desirable to empty and flush the infrared cell immediately after use and check the cell by its calibration with pure solvents.

Fig. 9 gives complete infrared spectrogram of butyl titanate in the range of 2 to 15 microns. The assignments in the different regions have been discussed below:

3.4 micron region: Fox and Martin[31,32] assigned the bands at approximately 2853 and 2872 cm^{-1} to symmetrical methyl and methylene groups and showed that the methyl band is intense in butyl alcohol and appears with enough dissymmetry on its low frequency side to suggest the possibility of another band. Pozefsky and Coggeshall[33] also reported four absorption bands at 2965, 2937, 2876 and 2853 cm^{-1} for normal butyl acetate, the last appearing

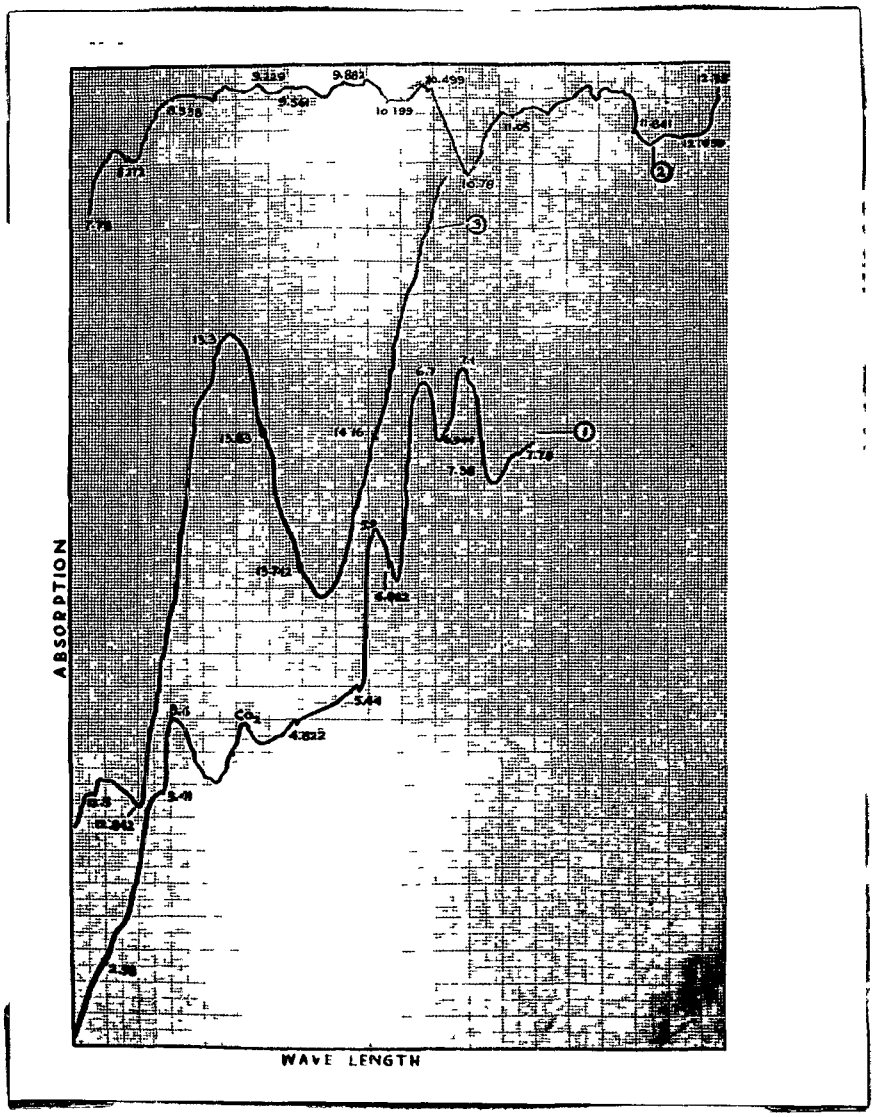

Fig. 9. Infrared absorption spectrum of tetra n-butyl titanate.

as a shoulder. These different bands are not shown in the spectrogram of butyl titanate. The only absorption peak at 3.4 micron shown by butyl titanate is due to the unresolved frequencies with different vibrational modes of $-CH_3$ and $>CH_2$ groups in the molecule. The broad and moderately strong band around 3125 cm^{-1} (3.2 micron) observed in titanyl hydroxide by Glemser[34] and Jere and Patel[30], characteristic of the hydrogen bonded metallic hydroxides is also observed in the spectrogram of butyl titanate.

5.5 - 7.3 micron region: The broad band in this region is due to deformation vibrations and C-O stretching vibrations in CH_2-CO groups.

8 - 10.5 micron region: In the course of the study on organosilicon compounds, Smith and McHard[35] have reported three peaks in this region at 8.4-8.8, 9.1-9.3 and 10.1-10.6 microns due to Si-O stretching vibration in Si-O-CH_2.R group. Wright and Hunter[36] stated that the bands involving Ti-O linkages are weak as compared to the bands arising of Si-O linkages. Recently Takatani, Yoshimoto and Moshillo[37] and Jere and Patel[30] have observed absorption bands in alkyl titanates in the region 8.3 to 10 microns which they attributed to the Ti-O bondings. Applying the same reasoning, five weak bands observed in butyl titanate at approximately 8.4, 9.3, 9.8, 9.96 and 10.46 microns may be assigned to Ti-O stretching vibration in -Ti-O-CH_2.R groups.

Distinct bands are shown at approximately 12.6 and 13.3 microns and diffused and weak bands in the region

10.8-11.7 microns. In comparison with the bands at 12.4 and 13.5 microns exhibited in the spectrum of normal butyl alcohol, it may be possible to assign 12.6 and 13.3 micron bands to C-H stretching and deformation vibrations. Another possibility is to assign these bands to skeletal vibrations of $-Ti-(O-C)_4$.

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PART II

BUTYL TITANATE AS A CATALYST FOR POLYMERISATION OF LINSEED OIL

INTRODUCTION

There are large number of naturally occurring oils which in raw state are capable of absorbing oxygen and forming a tough and solid insoluble film; such oils are termed drying oils. Drying oils like linseed, tung, fish, soybean and dehydrated castor, are used in varnish, paints and allied industries like linoleum and printing ink. Of these, linseed constitutes about 70 percent and for these purposes, the oil is polymerised or bodied and used. The polymerisation of the oil is usually done by heat treatment. To be used as a vehicle, it is necessary that the polymerisation is carried out in such a way that the oil does not develop dark colour, because oil with dark colour is not a desirable medium for surface coatings. This is usually achieved either by treating the oil for a long time in absence of air, or in presence of a suitable catalyst which brings about the desired extent of polymerisation in a very short period.

Polymerisation imparts many desirable properties to a drying oil. Besides, polymerised oils have better durability than unbodied oils, when used for paint formulations for outdoor exposure. Addition of oxygen when the oil is not polymerised is greater, which results in its degradation. The amount of oxygen taking part in the drying reaction in the case of polymerised oil is minimum and therefore, its stability is improved.

Cannegieter[38] observed that sulphur dioxide accelerates the bodying of linseed oil but has little effect on tung oil. As observed by Powers[39], aluminium chloride, boron fluoride and sulphuric acid greatly accelerate the polymerisation of drying oils, but the reaction is often difficult to control and leads to discolouration. Flakenburg and his co-workers[40] have studied the effect of anthraquinone and other polynuclear aromatic quinones on the polymerisation of linseed oil and have shown that these compounds promote the formation of conjugated structure.

No detailed study of butyl titanate as a catalyst for polymerisation of linseed oil has been made, however, Sidlow[41] while reviewing the developments of the organic derivatives of titanium has indicated the possibility of using butyl titanate as an agent for producing polymerised linseed oil. Experiments were, therefore, undertaken to investigate the suitability of butyl titanate as a polymerisation catalyst. A systematic study of the reaction with and without butyl titanate was made.

MATERIALS AND METHODS

Materials

Alkali refined, moisture free linseed oil with density 0.922 and having colour 1.2 yellow and 0.2 red units measured in 0.25" cell on Lovibond Tintometer was used.

Butyl titanate was prepared and the solvents used were spectrophotometric grade methyl alcohol supplied by

GMBH and Co., Munchen and S.P. grade butyl alcohol and carbon tetrachloride prepared by purification of C.P. reagents by the method described earlier.

Procedure

20 percent solution of butyl titanate weight by volume was prepared in butyl alcohol and 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 ml. of this solution were added to 100 ml. of linseed oil in each case to give 0.1 to 0.6 percent butyl titanate weight by volume. Mixtures were taken in 500 ml. Erlenmeyer flasks and were mechanically shaken for 1 hour to ensure homogeneous mixing. It was observed that the oil developed slight colour on the addition of butyl titanate.

About 60 ml. of the mixture were transferred to Pyrex boiling tubes (3 x 20 cm) and the level of the mixture in the tube was upto about 18.5 cms. The tubes were then immersed in an electrically heated liquid paraffin bath such that the tubes were not touching the base or walls of the bath and a constant temperature was maintained throughout the experiments. The samples were taken out periodically. Two sets of experiments were done at 200° and 250°C. At 200°C the samples were heated for 2, 4, 8, 12, 16, 24 and 30 hours and at 250°C, the samples were taken out after 1, 2, 4, 6, 8, 10, 12 and 16 hours. The samples were then cooled overnight to room temperature during which period the tubes were closed by velvet corks.

Methods of Evaluation

Many of the properties of drying oils change as they are polymerised. The density increases, the colour darkens, there is a change in the refractive index which increases in case of unconjugated oils and decreases in case of conjugated oils. But the most characteristic change is the increase in the viscosity. Changes in viscosity, colour and refractive index were selected as an index of extent of polymerisation. These were further followed up by infrared and ultraviolet absorption studies of the selected samples.

Viscosity: The viscosities of the samples heated at 200°C and 250°C were determined by Gardner's Bubble Viscometer and Stormer's Viscometer respectively.

Gardner's Bubble Viscometer: The instrument is based on the principle that the viscosity is directly proportional to the bubble speed. The viscosity of the sample is therefore determined by locating the standard tube in which an air bubble rises with the same speed as it does in a tube of the sample being tested. The bubble size of the sample is first adjusted as nearly as possible to that of the standard tubes and then the tubes are brought to a temperature of 27.5 ± 0.5°C by immersing them in a water bath for some time. The observation is made after the bubbles are completely formed which generally takes place about 1.5 to 2 cm. from the flat end of the tubes.

Stormer's Viscometer: Stormer's Viscometer is more accurate than the bubble viscometer. The apparatus may be briefly described as follows: A weight attached to string falls vertically. The string unwinds over a vertical pulley as the weight falls and causes a shaft to revolve. Thus the cylinder attached to its lower end is revolved, in liquid in the cup below. The whole instrument is so geared that a complete revolution of the needle on an indicator represents 100 turns of the cylinder in the cup below. A small water bath surrounds the container cup which enables temperature control to a reasonable extent. The revolution of the hollow cylindrical stirrer is resisted by the viscosity of the liquid. Thus if the viscometer is carefully calibrated with a liquid of known viscosity, it can be used to get accurate absolute viscosity values.

Calibration of Stormer's Viscometer: For calibrating the viscometer chemically pure glycerine diluted with freshly distilled water was used in making up a series of samples so that a range of concentrations from 60 to 99 percent was covered in increments corresponding to appreciable changes in viscosities. Nineteen sample solutions of 60 ml. each were prepared and stored in rubber corked 250 ml. Erlenmeyer flasks. These were shaken for about 2 hours by means of a mechanical shaker and left overnight. The glycerine sample was drawn up by means of a vacuum pump into a 50 ml. pipette previously rinsed with the same

Table 9

Calibration Data for Stormer's Viscometer

Percent glycerine in glycerine-water mixture by volume	Driving weight in grams	Time for 100 revolutions in seconds	Absolute viscosity in centipoises
60	30	12.2	8.015
65	30	13.6	11.10
70	30	15.6	15.96
75	30	19.3	24.47
80	30	26.2	40.00
80	50	16.8	40.00
82	50	18.6	49.30
84	50	20.8	62.00
86	50	24.5	79.00
88	50	29.3	104.00
90	50	35.7	137.30
90	120	16.5	137.30
91	120	18.1	158.80
92	120	20.3	185.60
93	120	22.8	217.70
94	120	25.7	255.80
95	120	29.2	301.80
95	150	23.3	301.80
96	150	26.2	357.60
97	150	30.8	428.40
98	150	35.3	514.40
99	150	41.5	629.00
100	150	50.5	764.00

solution. The outside of the pipette was then wiped to remove any adhering liquid and the pipette inverted in the viscometer cup. The water bath was kept at 27.5 ± 0.5°C. The calibration values are given in Table 9 and shown in Figs. 10 to 13. The absolute viscosity values

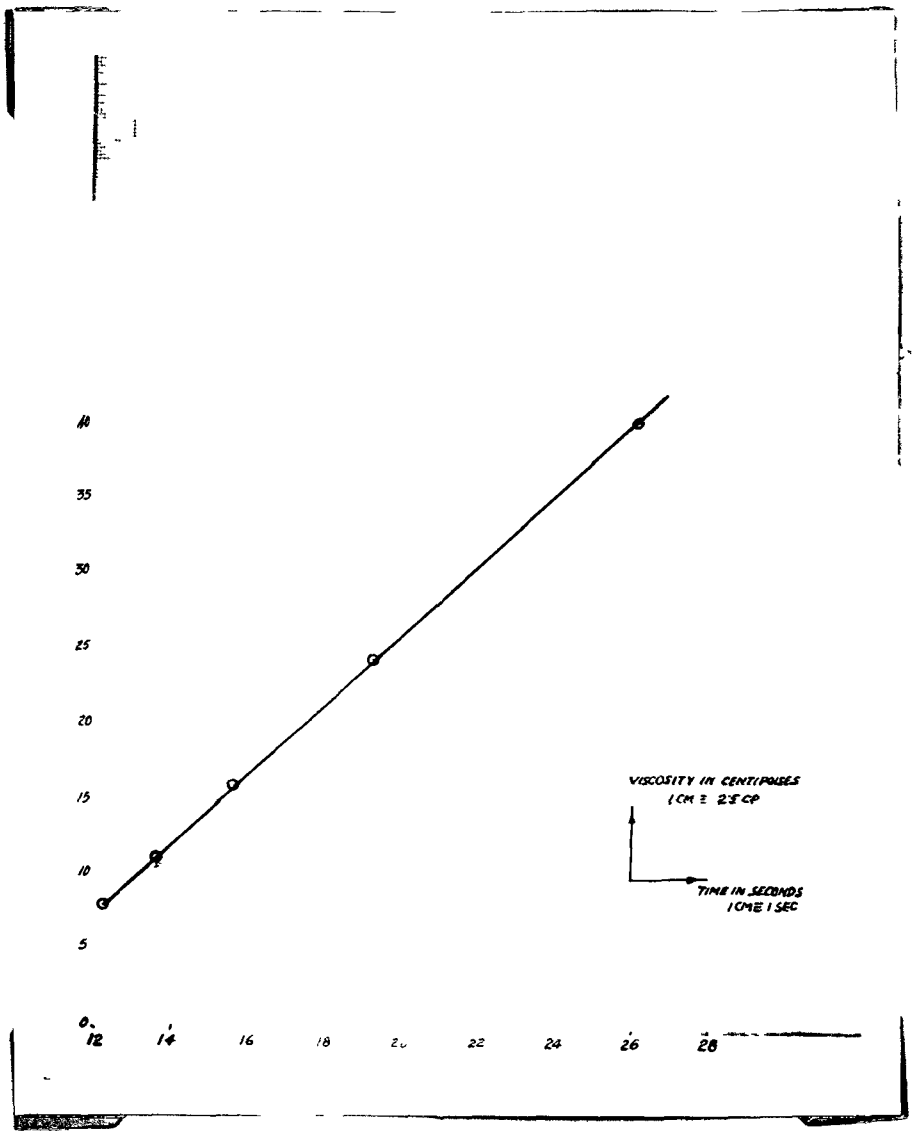

Fig. 10. Calibration curve for Stormer's Viscometer
Driving Weight 30 grams

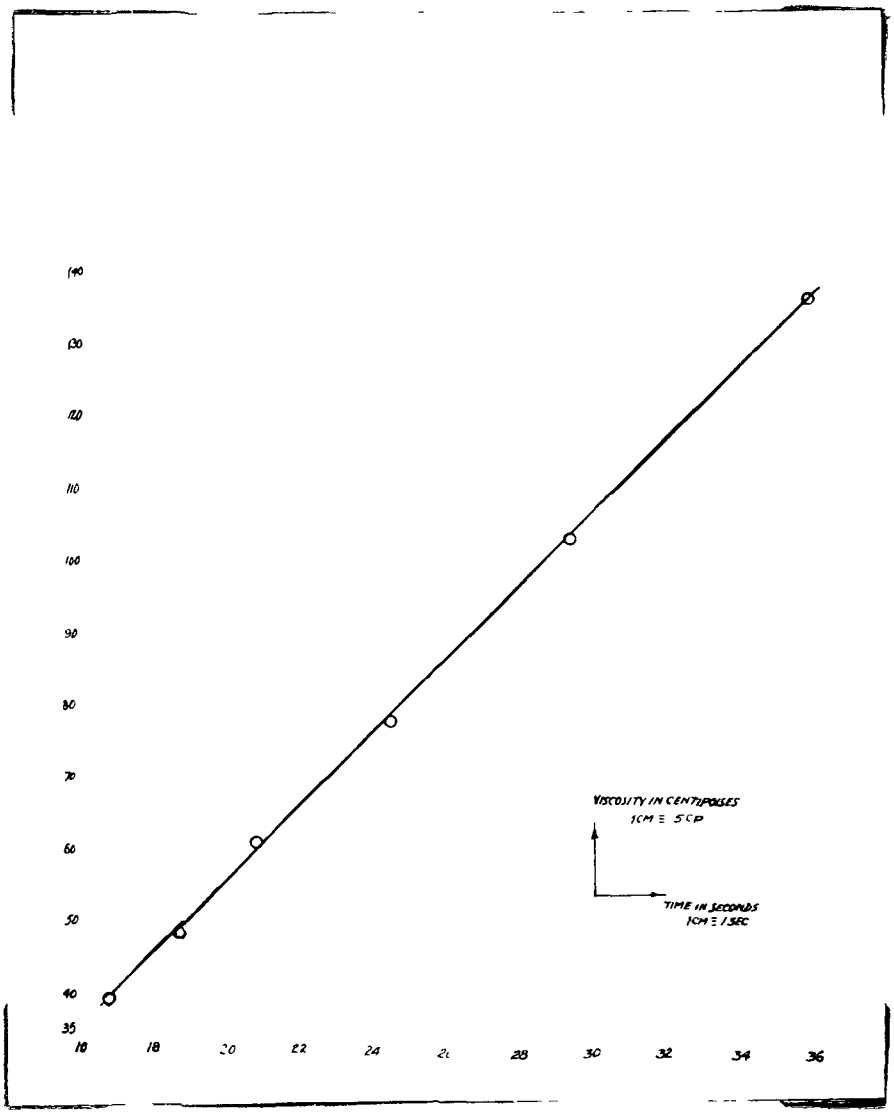

Fig. 11. Calibration curve for Stormer's Viscometer Driving Weight 50 grams

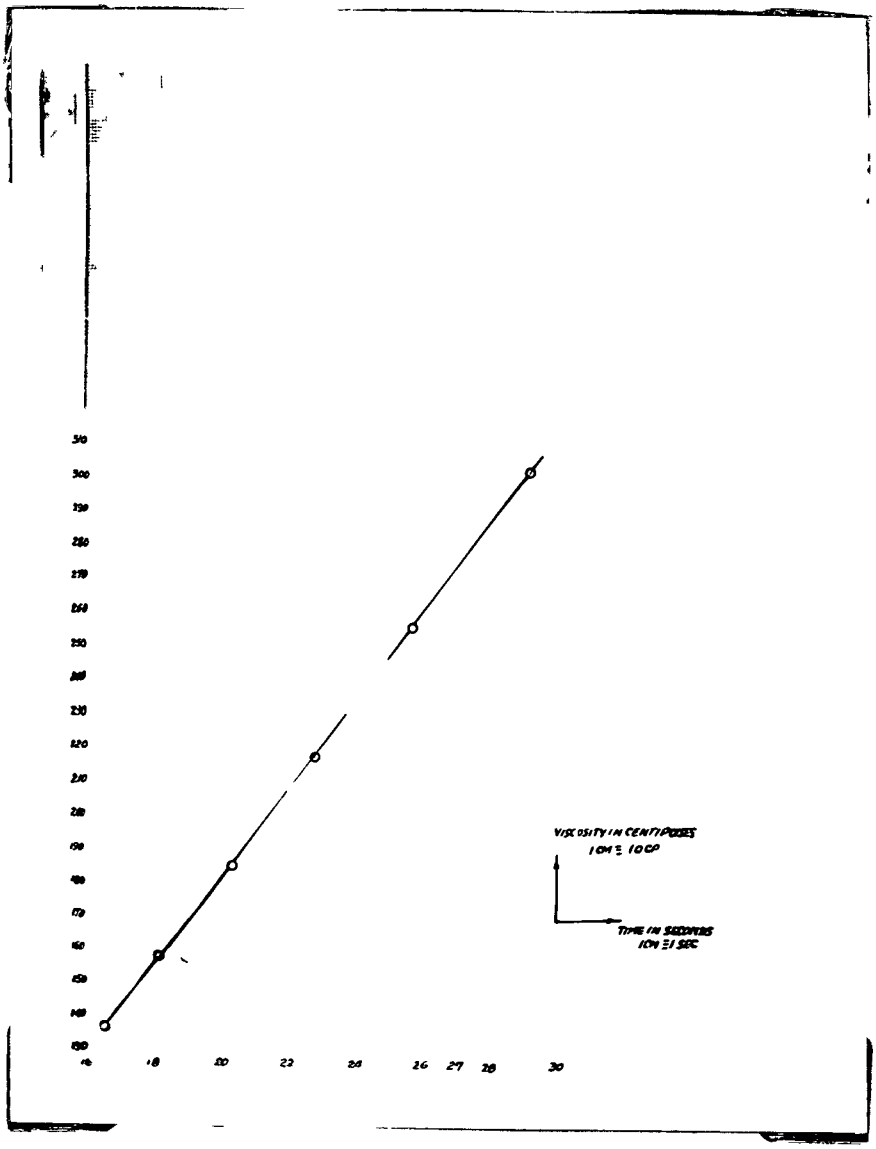

Fig. 12. Calibration curve for Stormer's Viscometer
Driving Weight 120 grams

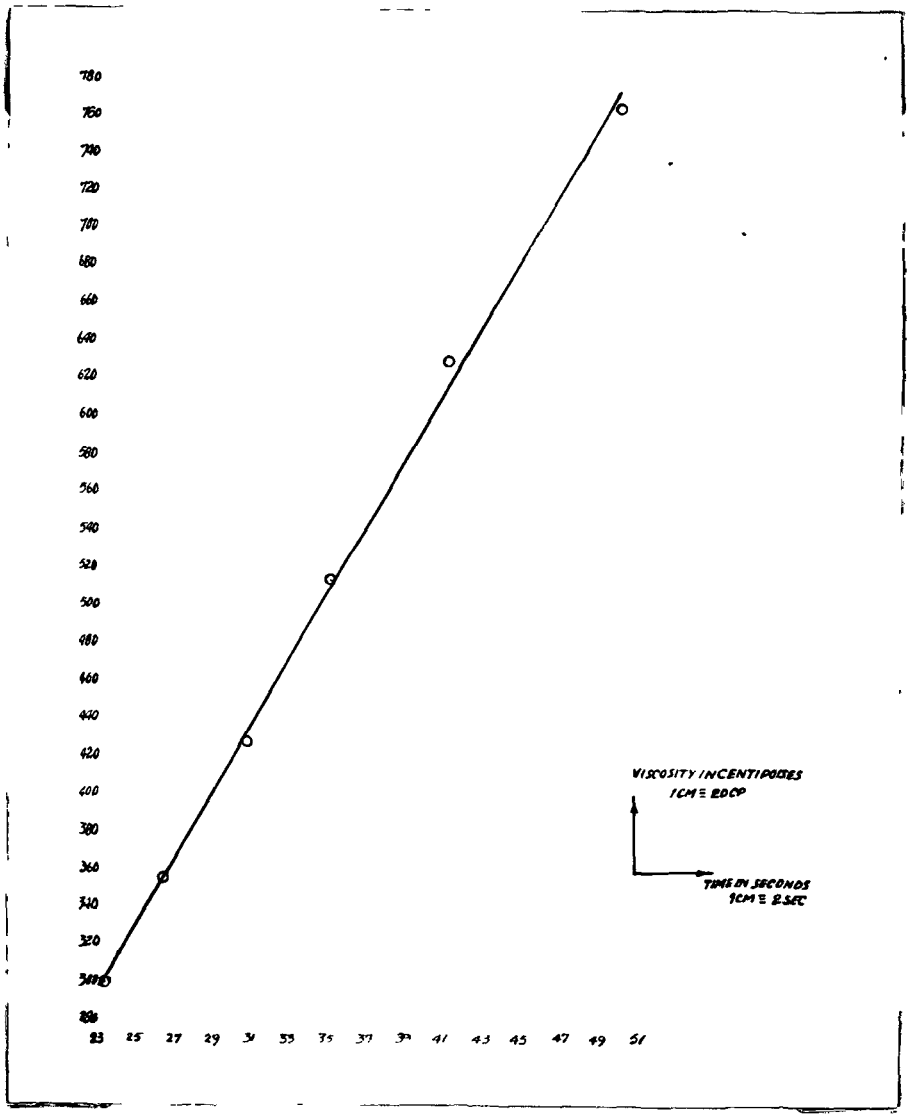

Fig. 13. Calibration curve for Stormer's Viscometer
Driving Weight 150 grams

for glycerine solutions were those of Sheely.[42]

Similarly the oil samples were run in the viscometer and the viscosity values were determined from the curves. Time was measured with a split second stop watch and the determinations were made in triplicate. Absolute viscosity values in centipoises were obtained using Gardner's Bubble Viscometer and Stormer's Viscometer for the oil sample heated at 200° and 250°C respectively.

Colour: Colour of the oil heated at 250°C was measured in Lovibond Tintometer using 1" cell after diluting the samples with chloroform in the ratio of 1:9. The results are calculated on Y+5R basis.

Refractive Index: Refractive index was measured at 30°C in Abbe's Refractometer using diffused daylight.

Infrared Absorption Spectra: 0.5 g. of oil was dissolved in 2.5 ml. of the S.P. grade carbon tetrachloride and the spectrogram was run in IR_2 recording type Beckman Spectrophotometer.

Ultraviolet Absorption Spectra: DU Beckman Spectrophotometer was used to determine the optical density of samples. The samples were prepared by dissolving the oil in S.P. grade methyl alcohol and diluting to such an extent that the final dilution was 0.135 g. per litre. Diene and Triene conjugation were calculated by using the formula $\frac{K233 \times 100}{92.1}$ and $\frac{K268 \times 100}{50.7}$ where K is the optical density.

D I S C U S S I O N

The main constituents of linseed oil are the glycerides of linoleic and linolenic acids. About 60 percent of the fatty acids of linseed oil is linolenic. It is probable that 40 percent of it consists of mixed linoleo-linolenins, containing for the most part of one saturated or oleic group and two polyethenoid acyl radicals which may be linoleic. Thus in linseed oil nearly all the triglyceride molecules contain at least one linolenic and one linoleic group, whilst many of them contain two of the diethenoid and one of the triethenoid radicals or vice-versa.

When linseed oil is heated in absence of oxygen at temperatures approaching 300°C, the iodine value commences to fall rapidly, i.e. a certain number of ethylenic linkages become saturated not by the addition of hydrogen or oxygen but by some kind of polymerisation effect. When the iodine value is about 100, the oil becomes somewhat but not very greatly viscous. When heating is continued at the same temperature, the iodine value declines further but not so markedly. However, the viscosity increases rapidly and the oil becomes thick although still quite clear. The effect of heat thus is to diminish the unsaturation and to increase the viscosity. Bradley and Richardson[43] and Stegor and Leon[44] studied heat treatment of linseed oil and ethyl linoleate and

showed that the polymerisation by heat of linoleic and linolenic groups is preceded by the rearrangement of their bonds to conjugated unsaturated linkings. The amount of conjugated unsaturation present in the thickened oils is very much less and it is postulated that the polymerisation has involved interaction or union at the conjugated unsaturated groups. The principal difference between normal linoleate and normal linolenate is that the linolenate develops conjugation and polymerisation more rapidly.[45] This is reasonable since linolenate has two active methylene between two double bonds while linoleate has only one.

The polymerisation of the conjugated isomers depends greatly on the cis-trans configuration. Paschke and Wheeler[45] have given the relative rates for linoleic and linolenic groups. Their results are given in Table 10.

Table 10

Effect of conjugation and cis-trans configuration on rate of polymerisation

Relative Speed	Conjugation	Number of Double bonds	Configuration
0.74	No	2	cis-trans
1.0	No	2	cis-cis
1.2	No	2	trans-trans
2.4	No	3	cis-cis-cis
5.8	Yes	2	cis-trans
26.0	Yes	2	trans-trans
170.0	Yes	3	cis-trans-trans
340.0	Yes	3	trans-trans-trans

The reason that trans-trans conjugated diene reacts more rapidly than cis-trans and cis-cis isomer in the Diels-Alder diene addition reaction is evident when one considers that a planar bent back or half ring or s-cis configuration is required for facile approach of the dienophile in a manner which will produce the cyclohexane ring of the adduct after reaction. It is difficult to describe but evident from inspection of scale models that trans-trans acylic dienes can most readily assume this planar s-cis configuration whereas the cis-trans diene shows some interference in assuming the configuration while the so far unknown cis-cis conjugated isomer has great interference.

Zechmeister[46] has also made certain observations regarding stearic hindrance in compounds containing three double bonds. He has shown that the central double bond of a conjugated system has the smallest amount of double bond character and that less activation energy is necessary for its isomerization. Of the three possible isomer the trans-cis-trans with a cis central bond shows the least stearic hindrance. The two alkyl groups of the resultant cyclohexadiene would be trans to each other about the ring. The cis-cis isomer exhibits the most hindrance and would give the same trans isomer. The cis-cis-trans and trans-cis-cis would give the cis isomer

Harrison and Wheeler[47] have demonstrated the ability of saturated long chain esters to link readily

and indicated the possibility that the linkages may occur at other sites in addition to those which involve diene system.

From the above discussion it is evident that the polymerising properties of drying oils will be modified by a catalyst like butyl titanate in so far as it affects the following factors:

1. The conjugated and non-conjugated unsaturation
2. The functionality of the double bonds, and
3. Cis-trans configuration of the double bonds.

The effect of butyl titanate on the polymerisation has been followed by changes in viscosity and colour. The conjugated and unconjugated unsaturation is measured by refractive index and by ultraviolet absorption at 233 millimicron and 268 millimicron. The infrared absorption was employed for determining the existence of the cis-trans isomers in the products obtained.

Viscosity: Varying amounts of butyl titanate 0.1 to 0.6 percent on the volume of linseed oil were added and the oil was heated from 2 to 30 hours at 200°C and 1 to 16 hours at 250°C. The results are given in Tables 11 and 12 and graphically shown in Figs. 14, 15 and 16. The viscosity of the oil heated in presence of 0.1 to 0.3 percent butyl titanate at 250°C for 16 hours conforms to the IS.79-1950 for light stand oil.

Sims[49] has established relationship between

Table 11

Change in viscosity on polymerisation of linseed oil at 200°C in presence of butyl titanate

Butyl titanate wt. % on vol. of oil	Viscosity in centipoises after hours.						
	2	4	8	12	16	24	30
0.0	40	40	50	100	115	200	245
0.1	40	40	85	115	140	215	315
0.2	40	40	85	115	140	320	415
0.4	40	40	85	115	140	285	345
0.5	40	40	85	115	140	250	315

Table 12

Change in viscosity on polymerisation of linseed oil at 250°C in presence of butyl titanate

Butyl titanate wt. % on vol. of oil	Viscosity in centipoises after hours.							
	1	2	4	6	8	10	12	16
0.0	41.75	43.25	62.75	87.00	99.50	105.25	110.00	144.00
0.1	41.75	50.50	67.25	109.50	133.00	171.00	287.00	942.00
0.2	41.75	54.50	83.00	117.00	148.50	216.50	322.50	568.00
0.3	43.25	53.50	64.75	101.00	137.00	180.00	294.00	505.00
0.4	43.25	50.50	69.25	95.25	115.00	180.00	253.75	404.00
0.5	44.00	49.50	60.50	94.50	96.50	139.50	213.00	358.00
0.6	42.25	50.50	63.75	83.50	107.50	136.00	180.50	272.00

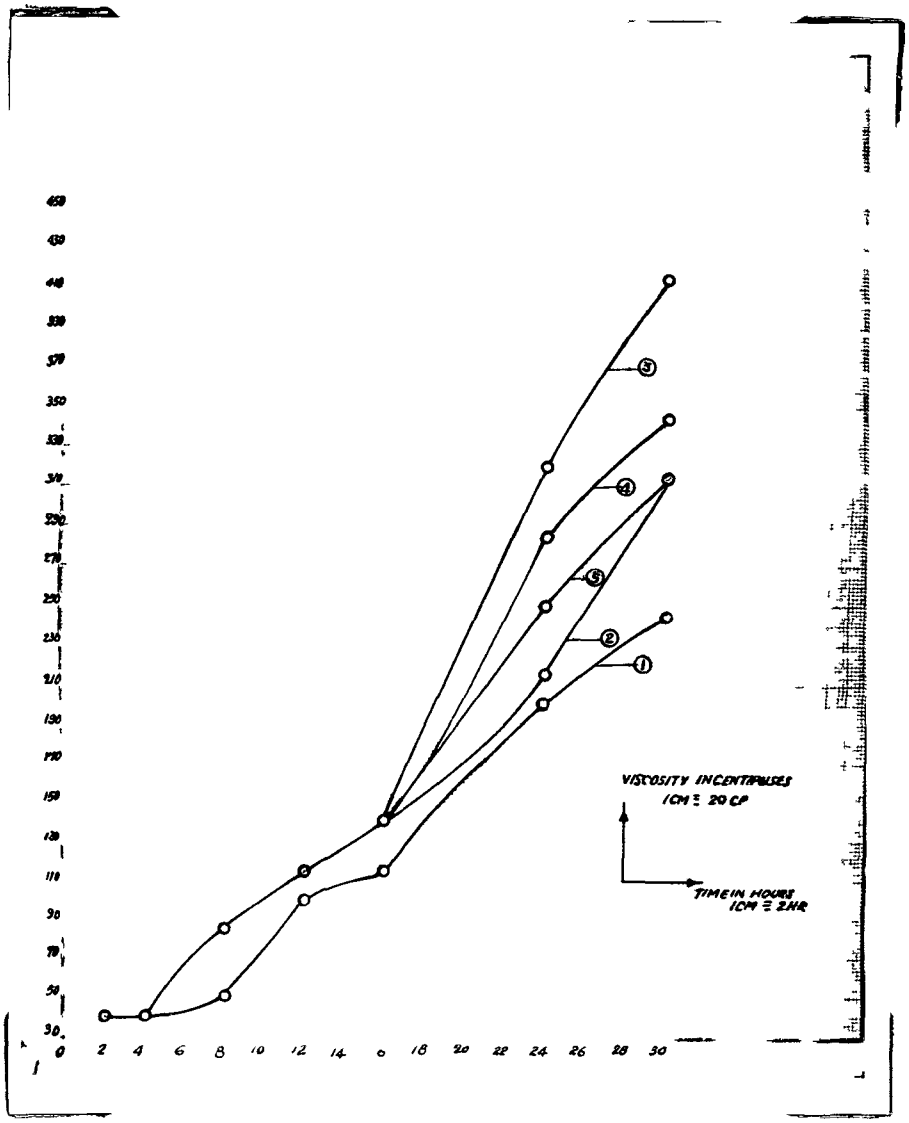

Fig. 14. Change in viscosity of linseed oil after heating at 200°C in presence of (1) nil, (2) 0.1, (3) 0.2, (4) 0.4 & (5) 0.5 percent butyl titanate.

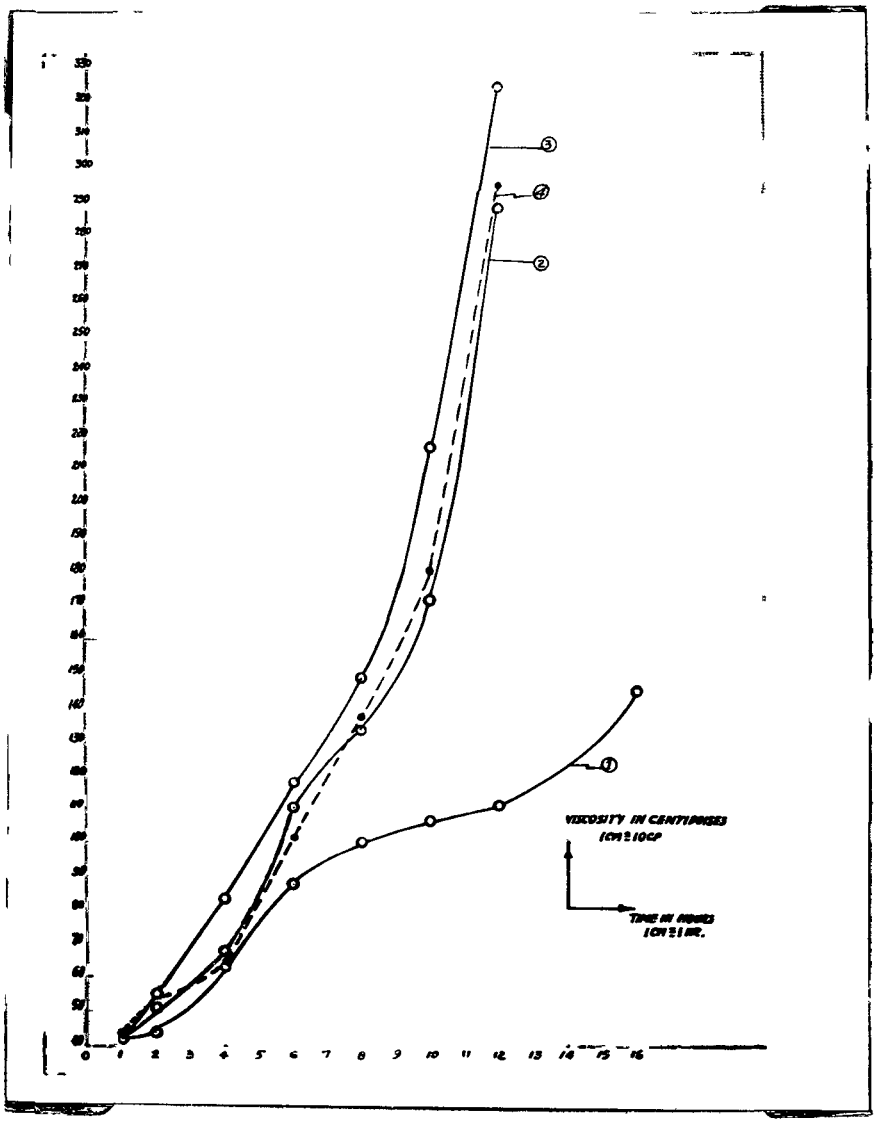

Fig. 15. Change in viscosity of linseed oil after heating at 250°C in presence of (1) nil, (2) 0.1, (3) 0.2 and (4) 0.5 percent butyl titanate.

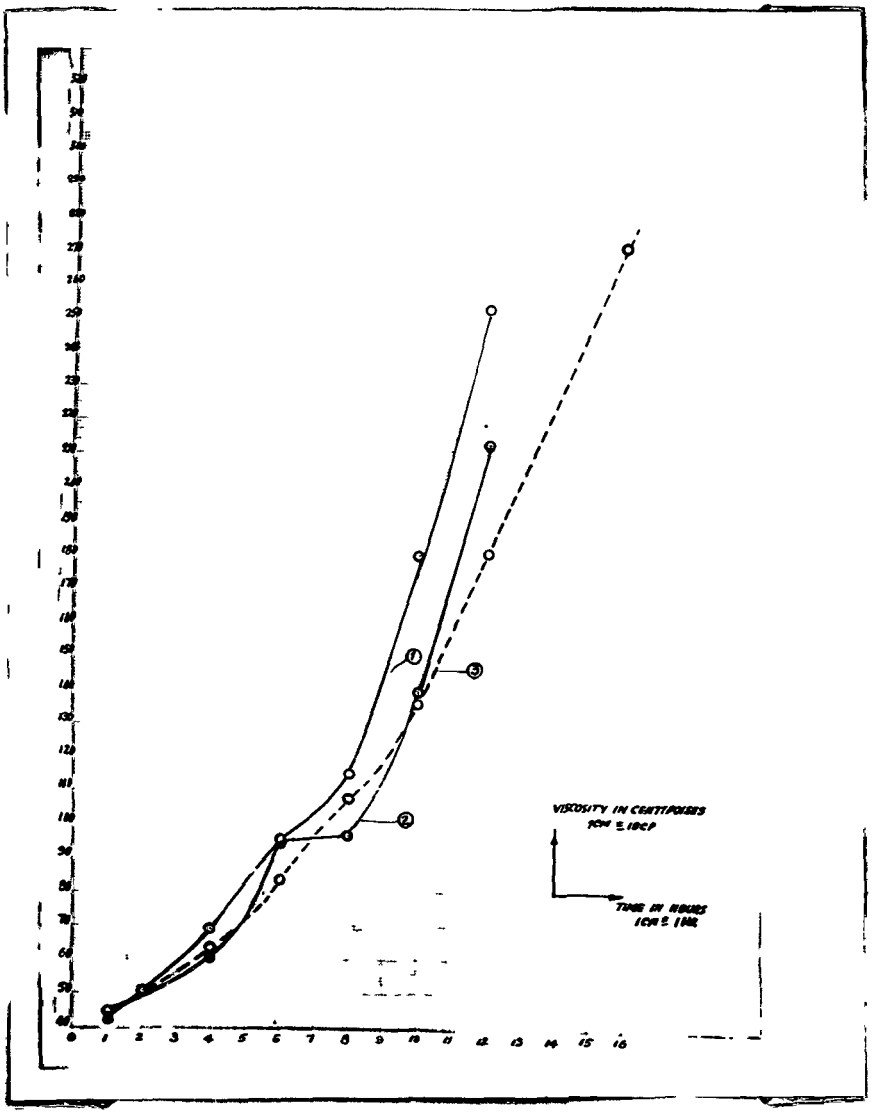

Fig. 16. Change in viscosity of linseed oil heated at 250°C in presence of (1) 0.4, (2) 0.5, and (3) 0.6 percent butyl titanate.

viscosity and polymerisation. Van Makusch[49] and Singleton and Johnson[50] observed three different sections in the plot of viscosity against time and concluded that linoleic acid polymerises more rapidly relative to linolenic acid in the second stage of the reaction than in the first; the effect of oleic acid is seen in the third or pre-gelation stage.

The plots of viscosity against time in the present study (Figs. 15 & 16) also show three portions when polymerisation of linseed oil is carried out at 250°C. The three portions are straight lines. The slope of the first and the third portions appears to be nearly the same, the middle portion which extends from 8 to 12 hours, in which the rate of polymerisation as shown by the slope of the curve is very slow when compared to the rate of polymerisation of the first and the third portions. On addition of butyl titanate, the tendency for the disappearance of the middle section is exhibited. The plot of viscosity against time for 0.2 percent butyl titanate shows only two sections, the first upto 8 hours and both being straight lines.

The behaviour of viscosity-time plots for the polymerisation at 200°C is similar but slope of the plot indicates that the polymerisation at 200°C is slow. At 200°C, the viscosity of linseed oil is not appreciably changed for the first 4 hours, subsequently it continuously increases on further heating. On addition of

butyl titanate also there is no change in the viscosity for 4 hours, the viscosity increases in the next 12 hours (from 4 to 16 hours) from 40 centipoises to 140 centipoises irrespective of the amount of butyl titanate added. Further increase after 16 hours, however, depends upon the amount of butyl titanate. The maximum effect is shown for 0.2 percent butyl titanate. There is nearly threefold increase in the viscosity with 0.2 percent butyl titanate whereas without butyl titanate, it is only doubled on heating after 16 upto 30 hours.

The linseed oil is polymerised to the same extent at 250°C in half the time as that at 200°C. Thus the viscosity reading at 250°C after 4 hours is equal to that at 200°C after 8 hours, that at 250°C after 6 hours is equal to that at 200°C after 12 hours and that at 250°C after 12 hours is equal to that at 200°C after 24 hours. It may be mentioned that Sidlov[41] has observed that at 300°C the polymerisation on heating in presence of 0.25 percent butyl titanate is very fast and gelation takes place in 4.5 hours. It was, therefore, considered that 250°C will be suitable temperature for the study of various reactions involved in the polymerisation and detailed investigation of the effect of butyl titanate on polymerisation of linseed oil at 250°C was made using various techniques.

The rate of change of viscosity on heating at 250°C with and without addition of butyl titanate is shown in Table 13. Without butyl titanate the rate from 2 to 8

Table 13

Rate of change of viscosity of linseed oil on heating at 250°C in presence of butyl titanate

Butyl titanate wt. % on vol. of oil	Rate per hour of change of viscosity during period					
	2 to 4 hrs.	4 to 6 hrs.	6 to 8 hrs.	8 to 10 hrs.	10 to 12 hrs.	12 to 16 hrs.
0.0	9.8	12.1	6.3	2.9	2.4	8.5
0.1	8.5	21.1	11.8	19.0	58.0	63.7
0.2	14.2	17.0	15.9	34.0	53.0	61.4
0.3	5.6	18.1	18.0	21.5	57.0	52.7
0.4	9.4	13.0	9.9	32.5	36.9	37.6
0.5	5.5	17.0	1.0	21.5	36.7	36.2
0.6	6.6	9.9	12.0	14.2	22.2	22.9

hours is nearly same as the rate between 12 to 16 hours; between 8 to 12 hours the rate is less than one-third of the above rates. On addition of butyl titanate the rate of polymerisation is nearly 1.5 to 2 times of that in the first 10 hours. The rate of change clearly shows a stepwise reaction with two stages in which reactions take place at constant rate with time lag in some cases between the completion of the first stage and commencement of the second stage. The average rates of change of viscosity in these two stages are shown in Table 14.

Table 14

Average rates of change of viscosity in the stagewise polymerisation of linseed oil at 250°C.

Butyl titanate wt. % on vol. of oil	Rate of change of viscosity in centipoises/hr. 2 - 6 hrs. V_1	10 - 16 hrs V_2	V_2/V_1
0.0	11	5.5	0.5
0.1	15	61	4.0
0.2	16	57	3.6
0.3	12	55	4.6
0.4	11	37	3.4
0.5	11	36	3.3
0.6	8	23	2.9

It will be seen that in both the stages the rates increase on addition of butyl titanate, they are maximum for 0.1 to 0.3 percent butyl titanate and decrease with

further increase in the proportion of butyl titanate. As suggested by Singleton and Johnson[50], it is believed that these two stages represent linear polymerisation followed by three dimensional polymerisation. The rate of change of viscosity in the second stage is nearly three to four times of that in the first stage. The fact that the rates of change of viscosity in case of linseed oil alone in the first and final stages are nearly the same shows that in both the stages it is linear polymerisation and only dimers are formed. When butyl titanate is added dimers are formed in the first stage and polymers involving three to four molecules are formed in the second stage. On addition of butyl titanate in higher proportions a different mechanism sets in which interferes with the formation of high polymers.

Butyl titanate can act as a catalyst for the process of conjugation of double bonds in linoleic and linolenic acid components of linseed oil. The polymerisation takes place at the double bonds. Wheeler[51] has shown that when the polyethenoid ester is conjugated, the dimerisation reaction takes place as follows by Diels-Alder addition reaction with one molecule functioning as dienophile (Fig. 17). Trimers may be formed by a double bond of the dimer acting as dienophile and another molecule of conjugated ester acting as diene. The non-conjugated ester also can act as dienophile and can form dimers by adding to the double bond of another conjugated

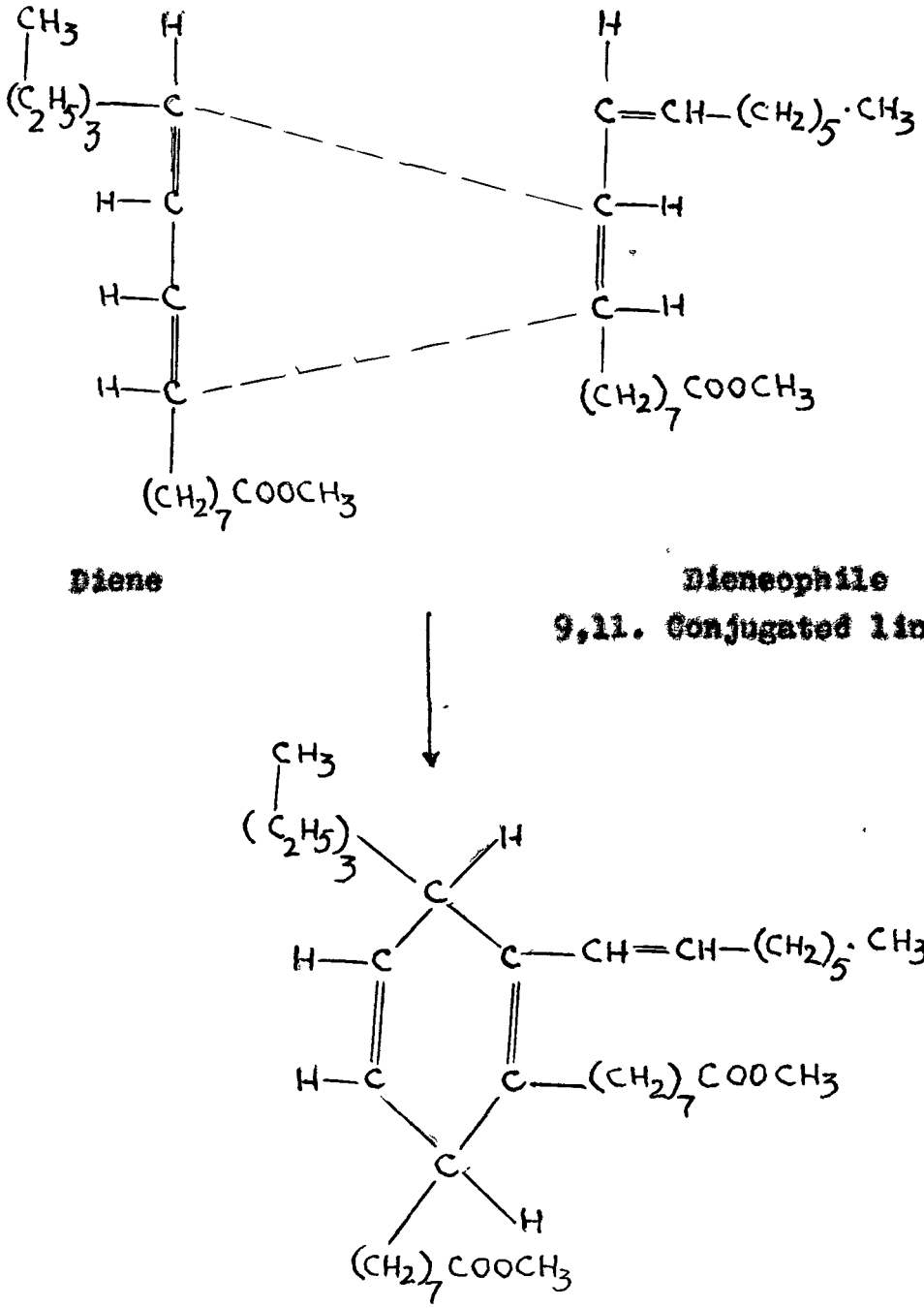

Fig. 17. Adduct: A dimer of linoleate

ester which acts as the diene . The change of the non-conjugated bonds to conjugated bonds is slow and the rate of this process determines the rate of polymerisation. The following mechanism is suggested by which butyl titanate catalyses the shift of the non-conjugated form to the conjugated form in the linseed oil. It is postulated[40] that the isomerisation occurs by means of a prototype shift and this in case of butyl titanate and linoleic acid is shown in Fig. 18.

The higher polymer formation is related to double bond functionality. In a mono-functional system the monomer has a functionality of one and it can form only a dimer with another molecule of a monomer. In a system with high functionality the monomers combine to form dimers, the functionality of each monomer is reduced by only one, so that the resulting dimer still has a functionality of two in bi-functional system and four in tri-functional system. The dimer can then react with another monomer or dimer to form trimers or tetramers still having further functionality. The reactions can thus continue to very high polymers. Theoretically polymers with infinite molecular weight can be formed at complete reaction. The greater the functionality the greater is the average molecular weight and tendency to form extensive gels of high molecular weight.

Viscosity data indicates that effective double bond functionality is maximum on addition of 0.2 percent

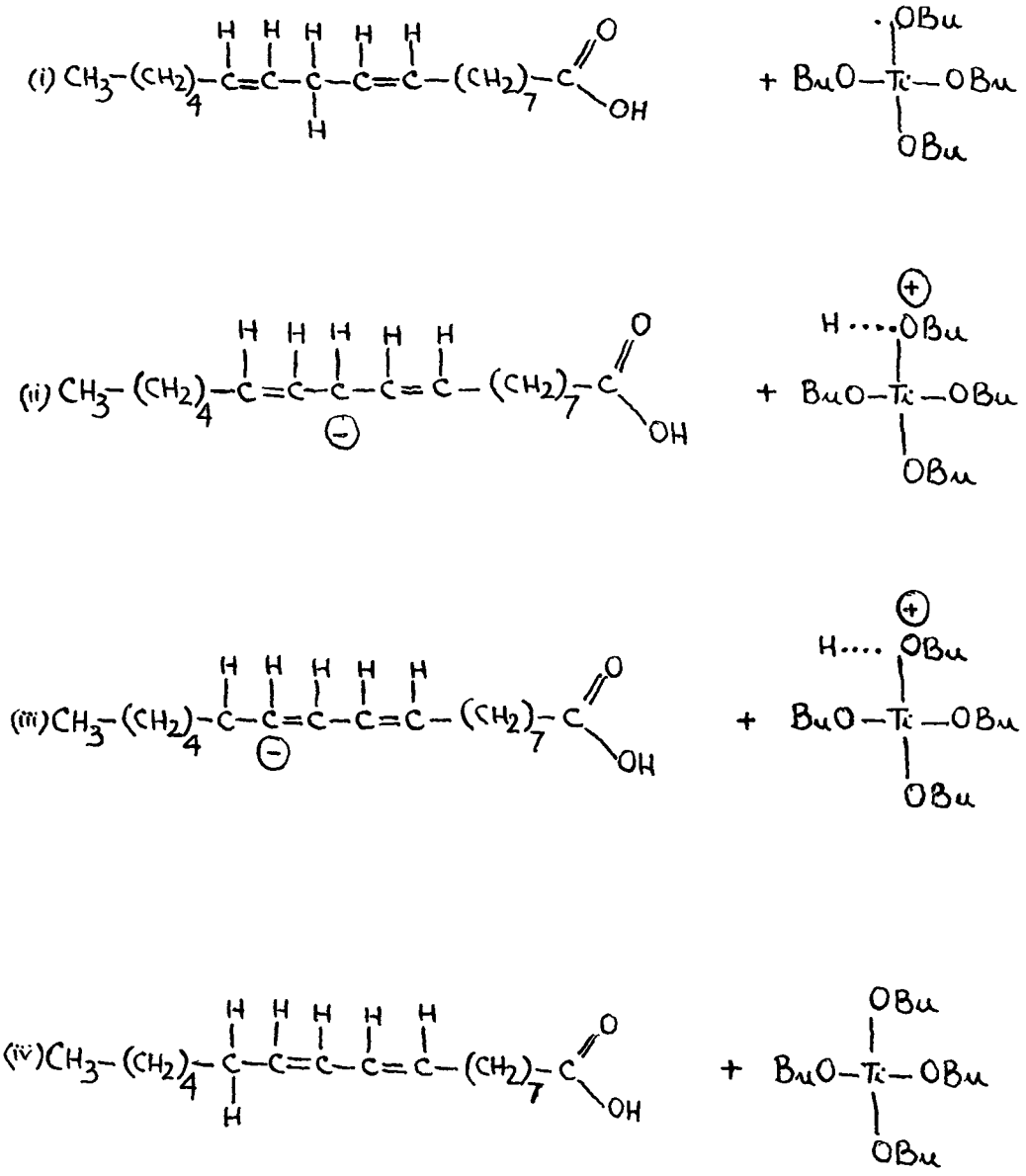

Fig. 18. Conjugation of linoleic acid in presence of butyl titanate

butyl titanate and it decreases with increase in the proportion of butyl titanate. The refractive index, ultraviolet and infrared absorption values discussed later suggest that in case of polymerisation reactions with higher proportions of butyl titanate, the arrangement of the double bonds in relation to one another is different, the number of conjugated double bonds is less but the extent of unsaturation is more. This can be explained by assuming dimerisation by addition of conjugated double bond to a non-conjugated double bond. The double bond functionality in this case will be less than when the dimerisation takes place by addition reaction between two conjugated double bonds. This is due to the preponderance of non-conjugated and cis isomers which polymerise very slowly.

Colour: The effect of butyl titanate on colour of linseed oil heated at 250°C is shown in Table 15 and Figs. 19 & 20. It will be seen that the conclusions from the colour changes are not as definite as these made from the viscosity readings. However, the following general observations can be made:

(1) The colour changes gradually with time,

(2) The plots of colour versus time show different sections but these do not generally correspond with the sections in the plots of viscosity against time.

(3) In presence of butyl titanate the plots can be divided into two distinct sections, the rate of colour

Table 15

Change in colour on heating linseed oil at 250°C in presence of butyl titanate

Butyl titanate wt. % on vol. of oil	Colour on Y+5R basis of the oil diluted ten times after hours.							
	1	2	4	6	8	10	12	16
0.0	2.0	2.0	2.3	4.7	5.4	6.7	7.3	13.5
0.1	11.5	12.7	14.5	15.5	19.5	20.5	41.5	50.5
0.2	14.2	19.7	23.0	17.5	35.0	39.5	48.0	58.0
0.3	18.8	21.5	22.0	23.5	34.0	38.0	42.5	59.0
0.4	20.9	23.0	24.5	28.5	36.0	40.5	48.0	65.0
0.5	21.5	24.5	29.0	35.0	43.5	48.5	60.0	87.0
0.6	22.2	23.4	33.5	33.0	48.0	50.5	74.5	96.0

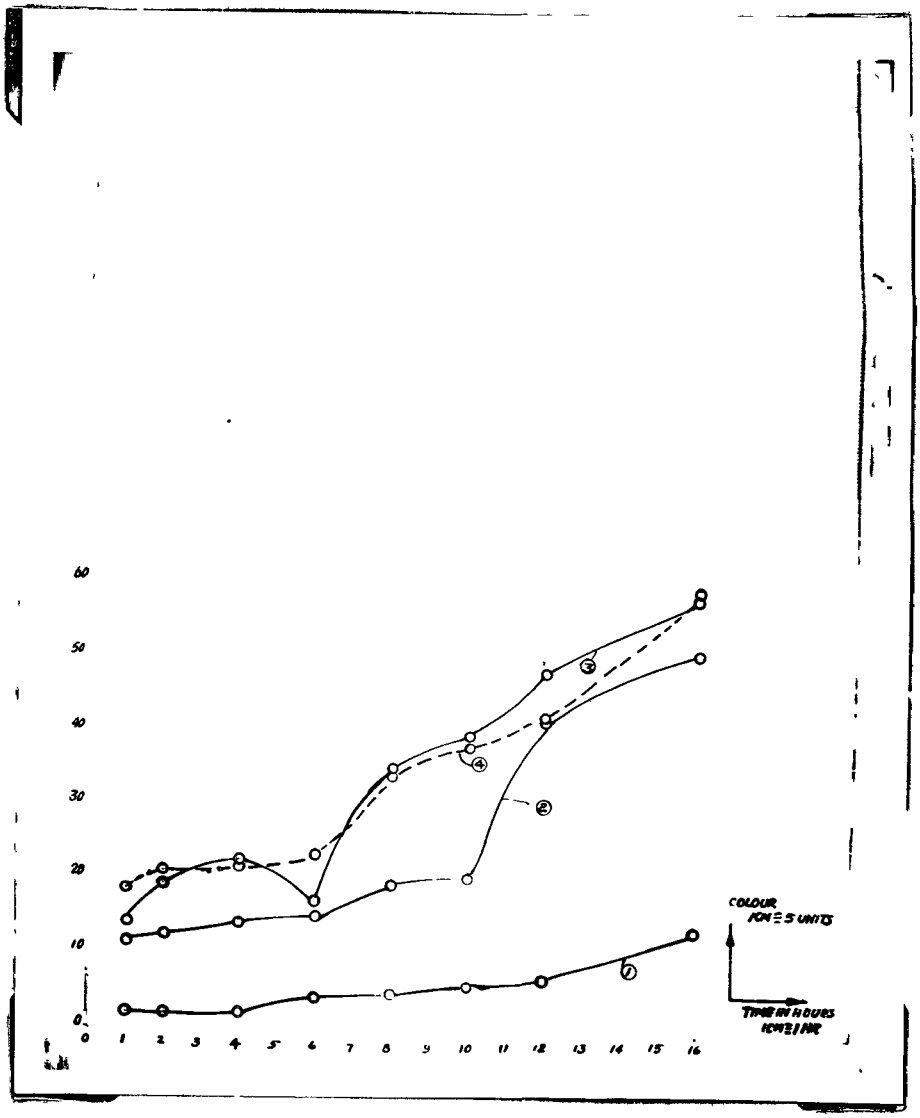

Fig. 19. Change in colour of linseed oil heated at 250°C in presence of (1) nil, (2) 0.1, (3) 0.2 and (4) 0.3 percent butyl titanate.

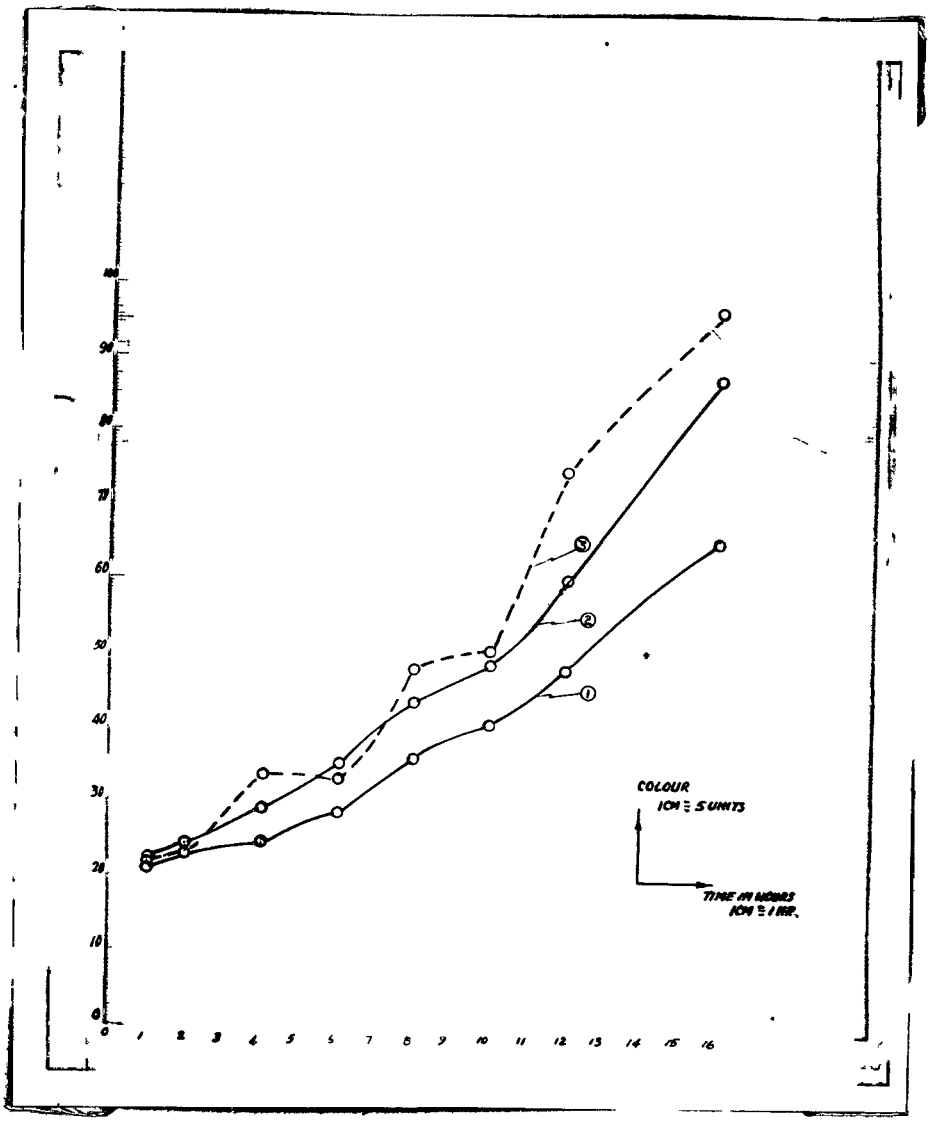

Fig. 20. Change in colour of linseed oil heated at 250°C in presence of (1) 0.4, (2) 0.5 and (3) 0.6 percent butyl titanate.

change in the first section being comparatively slower than in the second section.

(4) The colour increase is more when the oil is heated in the presence of butyl titanate. When the optimum proportion of butyl titanate (0.2 percent) is added, the colour increase in the first section is gradual upto ten hours. On further heating, the colour reading is nearly doubled in the next two hours (10-12 hours). The optimum conditions for obtaining a drying oil of desired viscosity and minimum colour thus appear to be addition of about 0.2 percent butyl titanate and heating at 250°C for ten hours.

(5) With higher proportions of butyl titanate, the polymerisation as shown by viscosity is less than with 0.2 percent butyl titanate and also the oil is darker.

(6) The colour in oils is due to the presence of (i) carotenoids ranging in colour from yellow to deep red, (ii) chlorophyll which imparts greenish tinge to the oil and (iii) some other compounds which develop colour on oxidation. It is probable that increase in colour on addition of butyl titanate is due to oxidising action of the titanate on the colour bodies. The oxidising action is more pronounced (a) when butyl titanate is added in greater proportion than the optimum (0.2 percent) and (b) with 0.2 percent butyl titanate in the advanced stages of polymerisation (after 10 hours) when it ceases to function as catalyst for polymerisation of linseed oil and is

available for the oxidation reaction.

So it can be easily seen that final colour of the drying oil can be controlled (i) by removing the colour bodies susceptible to oxidation from the original oil, (ii) by adding requisite proportion of butyl titanate and (iii) avoiding the heating of the linseed oil beyond the stage when further colour increase is rapid.

Infrared Absorption: O. Neill and Cole[52] have described the infrared spectrum of linseed oil. The spectrogram obtained and reproduced in Fig. 21 agreed with this. The main bands and their assignment given by them are as follows: (1) the absorption at 3.5 micron arises from the C-H valence vibrations of the methyl and methylene groups, (2) the single strong absorption band at 5.74 microns is characteristic of the valence vibration of the ester group, (3) the peaks at 7.0 microns are connected with deformation vibrations of the methyl and the methylene groups, (4) the bands in the 10 micron region are due to C-H deformation about the ethylene group and (5) the strong absorption near 14 micron arises from the CH_2 rocking vibration of the long aliphatic chains together with the unresolved contribution of the double bonds of the oil. The region of the unsaturated groups which occurs towards the centre of the fatty acid chain appears to make little characteristic contribution.

The infrared spectra of linseed oil heated at 250°C with and without butyl titanate have been given in

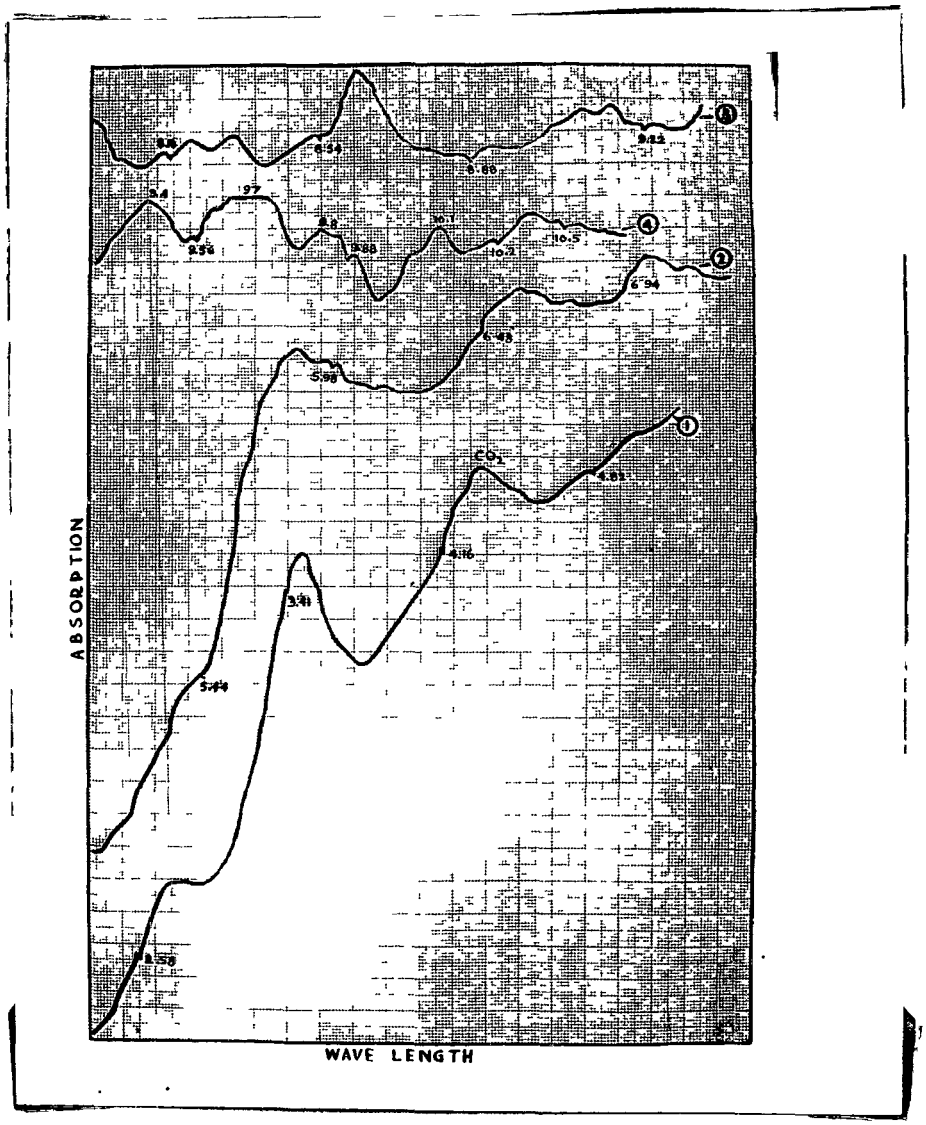

Fig. 21. Infrared absorption spectrum of linseed oil.

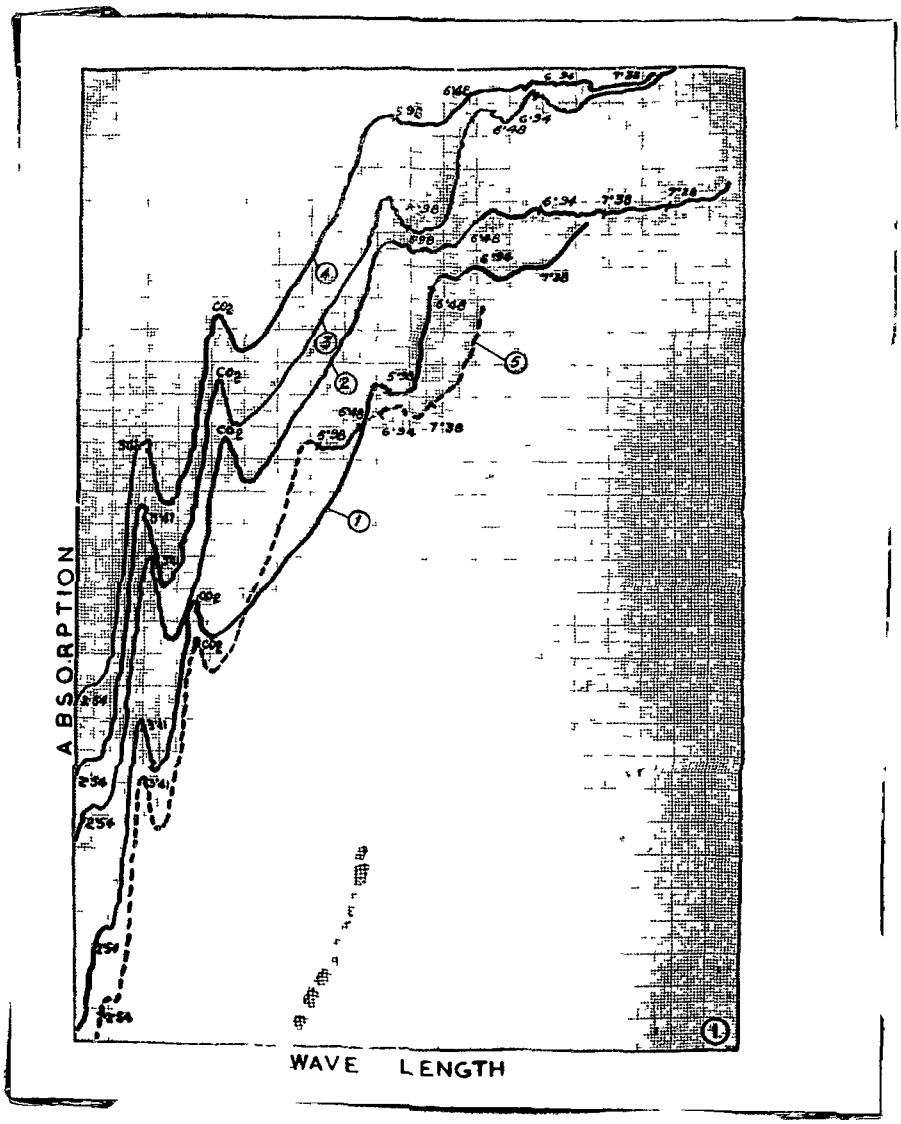

Fig. 22. Infrared absorption spectrum of linseed oil (2-8 microns) heated for (1) 2, (2) 4, (3) 6, (4) 8 and (5) 10 hours.

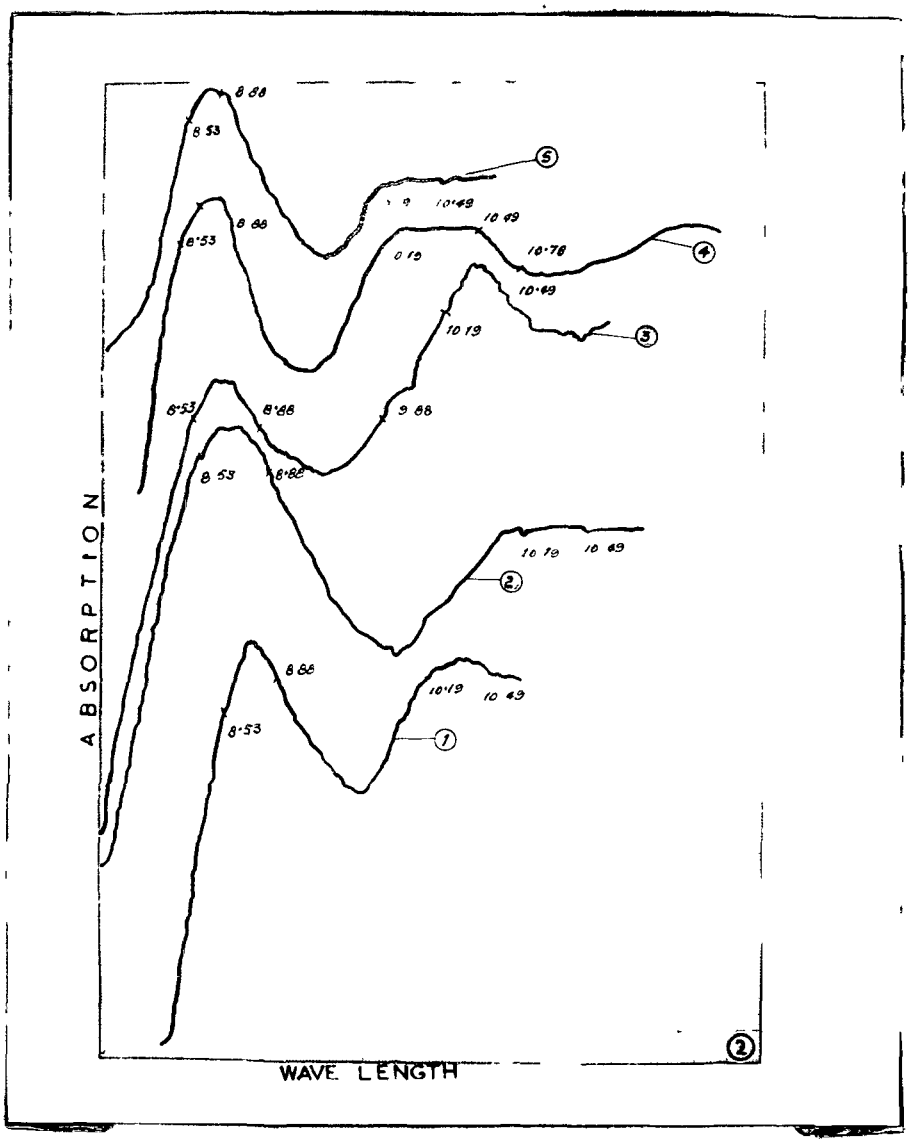

Fig. 23. Infrared absorption spectrum of linseed oil (8-10.5 microns) heated for (1) 2, (2) 4, (3) 6, (4) 8 and (5) 10 hours.

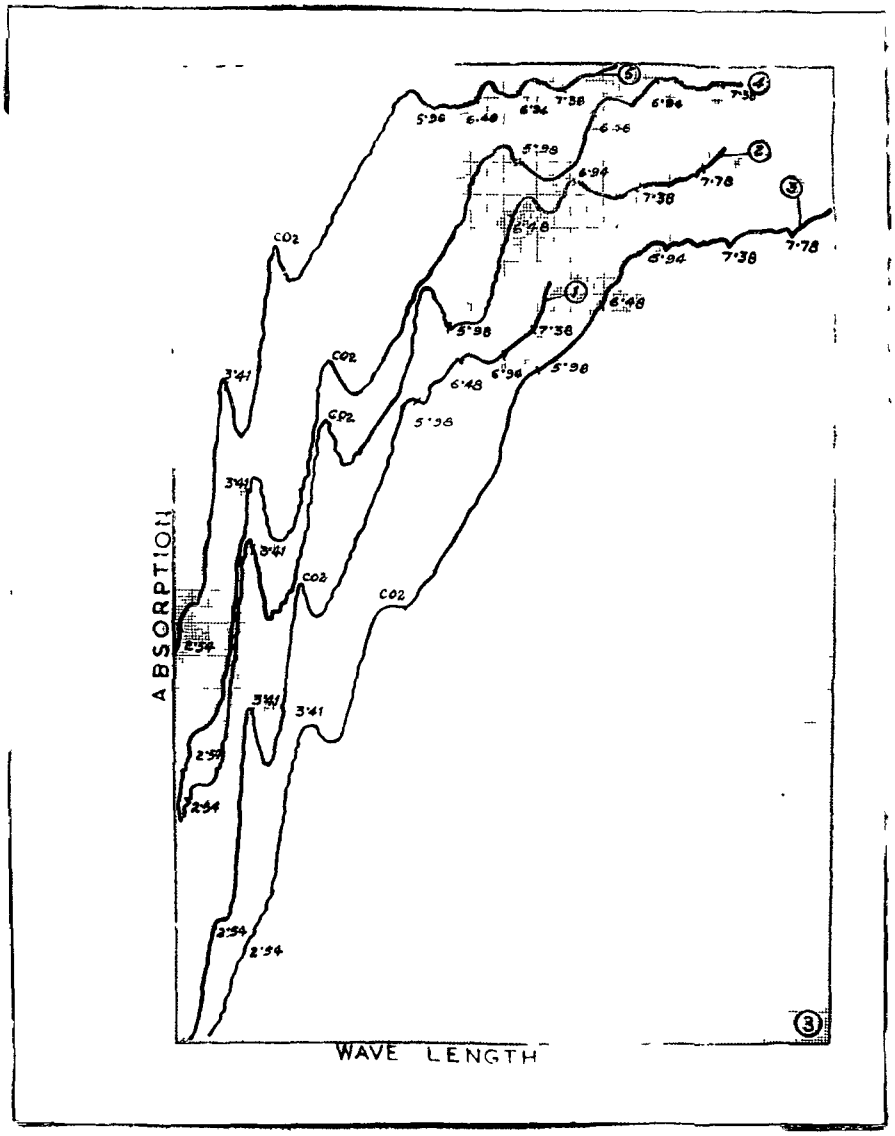

Fig. 24. Infrared absorption spectrum of linseed oil (2-8 microns) heated in presence of 0.2 percent butyl titanate for (1) 2, (2) 4, (3) 6, (4) 8 and (5) 10 hours.

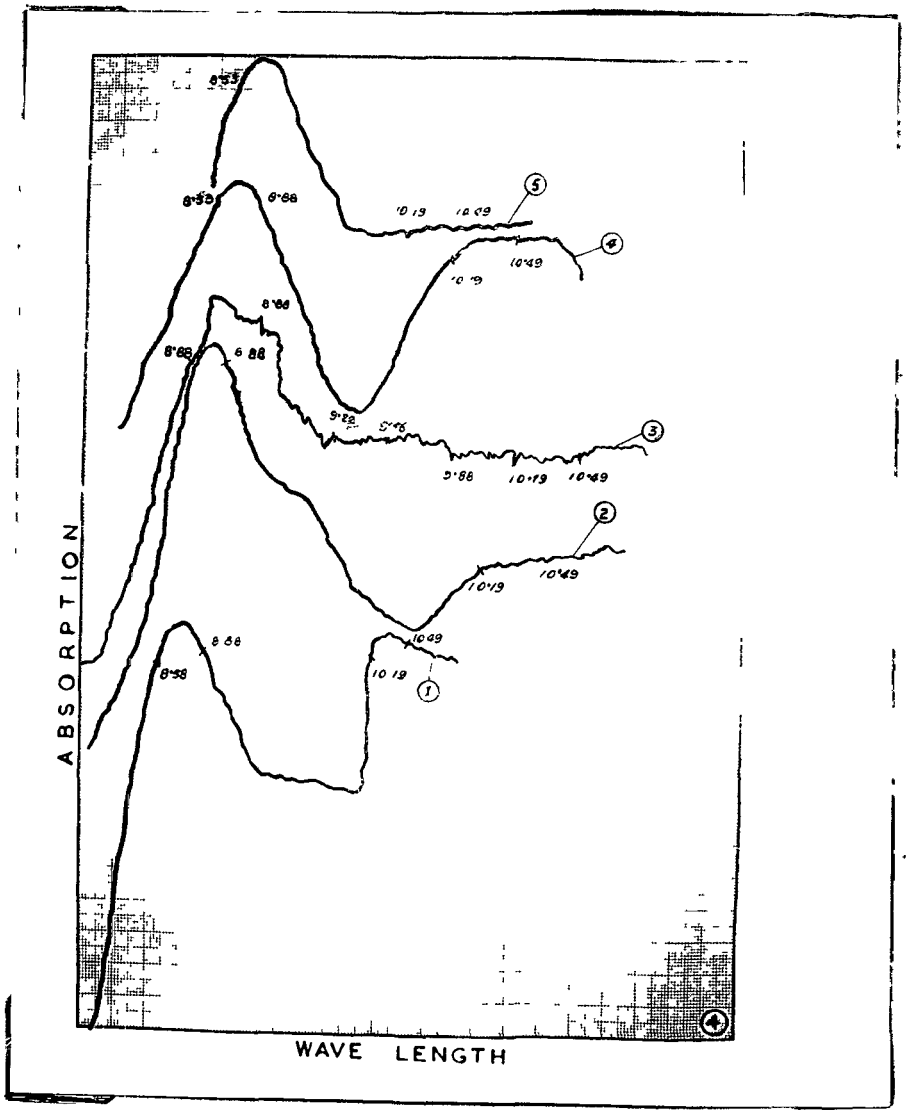

Fig. 25. Infrared absorption spectrum of linseed oil (8-10.5 microns) heated in presence of 0.2 percent butyl titanate for (1) 2, (2) 4, (3) 6, (4) 8 and (5) 10 hours.

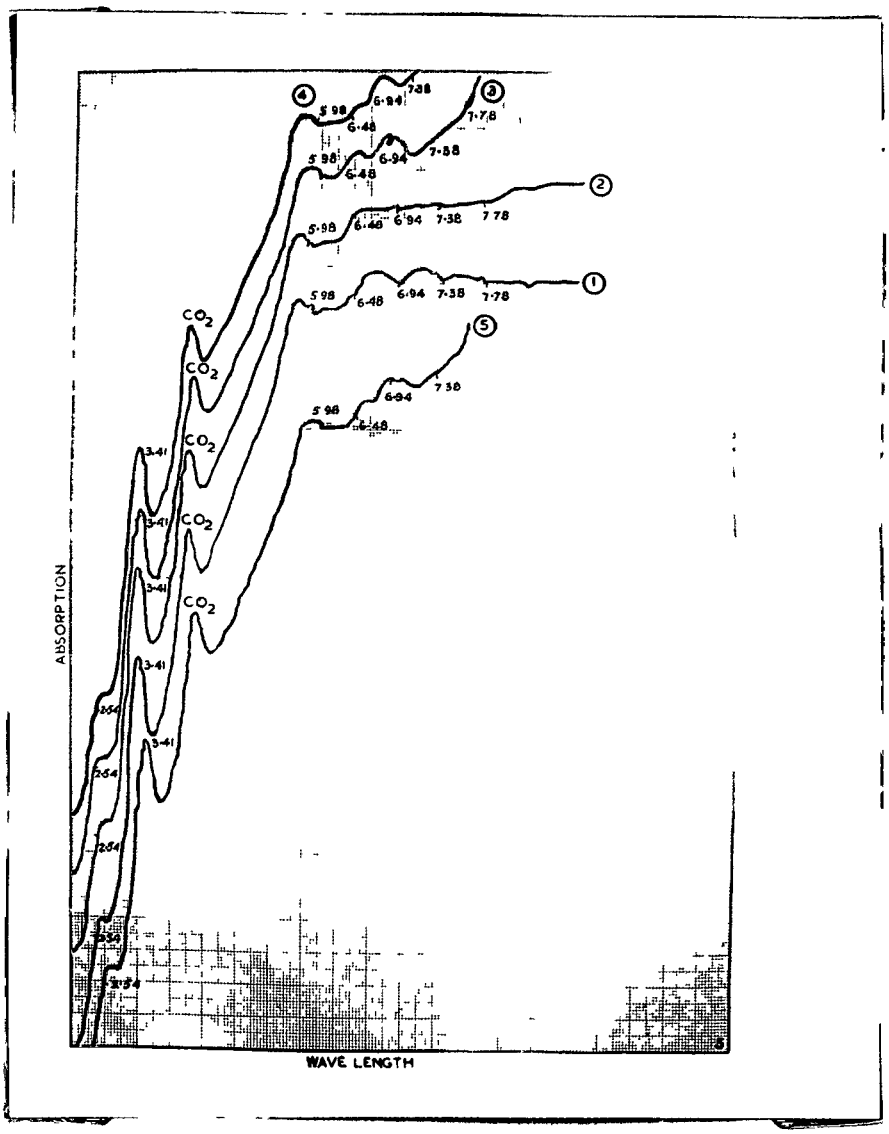

Fig. 26. Infrared absorption spectrum of linseed oil (2-8 microns) heated for 10 hours in presence of (1) 0.1, (2) 0.3, (3) 0.4, (4) 0.5 and (5) 0.6 percent butyl titanate.

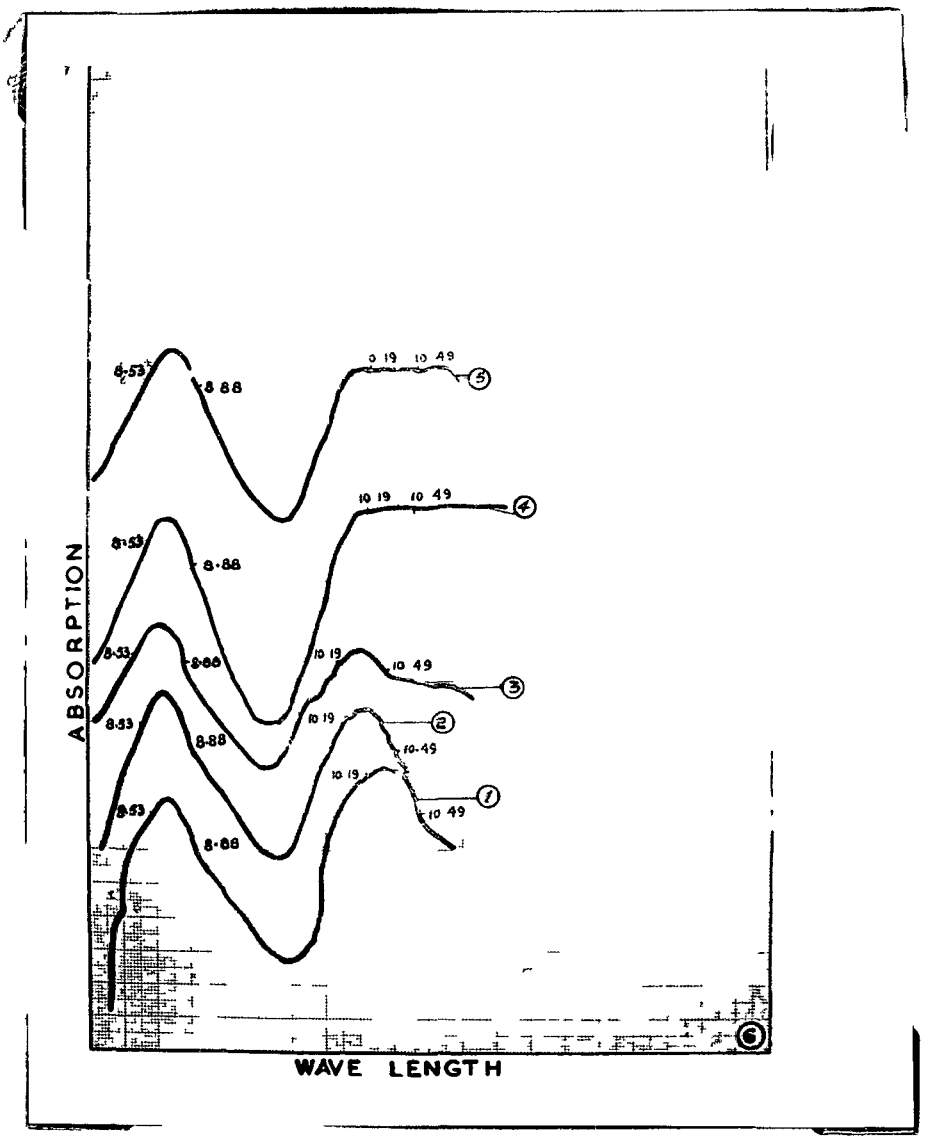

Fig. 27. Infrared absorption spectrum of linseed oil (8-10.5 microns) heated for 10 hours in presence of (1) 0.1, (2) 0.3, (3) 0.4, (4) 0.5 and (5) 0.6 percent butyl titanate.

Figs. 22 to 27. The effect of polymerisation on different absorption bands is discussed below.

3.5 micron region: The peak areas show increase in intensity during the first stage of polymerisation. They decrease in the second stage finally attaining the same value as that of the original oil. The increase in the peak areas in the first stage is generally greater when the polymerisation is carried out without butyl titanate.

The comparison with the results of previous workers[52,54,55,56] indicates that this peak may be due to C-H stretching in $-CH_3$, $>CH_2$, $>CH$ and $=\overset{|}{C}H$ or $=CH_2$ groups. The increase in absorption intensity in the first stage and decrease when three dimensional polymerisation sets in suggests that the C-H stretchings are affected by conjugation, cis-trans isomerisation and saturation by polymerisation of the double bonds. The peak areas give an indication of the unutilised double bond functionality. The maximum peak area is nearly three times of the peak area in the initial stages of heating. This is explained by the fact that in linseed oil on conjugation three conjugated dienes are possible. On polymerisation the dienes get saturated and the peak area decreases.

6 micron region: The 5.8 micron band is due to the carbonyl group in the ester. The infrared spectra of the polymerised linseed oil under various conditions generally show that the peak at 5.8 micron band is broad and unresolved. Sharp peaks are obtained when the polymerisation

is carried out in the presence of optimum proportion of butyl titanate (0.2 percent). Also sharp peak is obtained in the last stages of the linear polymerisation step when the reaction is carried out with butyl titanate.

7 micron region: The absorption bands in this region are broad, unresolved and weak in original as well as polymerised linseed oil.

5.6 - 5.8 micron region: The absorption bands in this region are presumed to be characteristic of the glycerol part of the molecules. The intensity of the peak is minimum in the last stages of the linear polymerisation step. Also there is a tendency of diminution of these peaks in proportion to the polymerisation at the end of the second stage.

10 micron region: The bands in the 10 micron region are due to C-H deformation about the ethylene group. In linseed oil the double bonds are non-conjugated and exhibit weak absorption intensity. The characteristic wavelength positions for different cis-trans configurations are as follows:[57] 10.53 micron cis-trans conjugated, 10.34 micron isolated trans, 10.17 micron cis-trans conjugated, 10.12 micron trans-trans conjugated, 10.11 micron cis-cis-trans conjugated, 10.09 micron cis-trans-trans conjugated and 10.06 micron trans-trans-trans conjugated.

In the original oil, the bands are non-conjugated and of cis configuration which are weak in intensity.

On heating an intense band at 10.34 micron appears and increases in its intensity. This band is due to trans double bonds formed by isomerisation of the cis bonds of the oil. The absence of distinct 10.17 and 10.53 micron peaks may indicate absence of any high concentration of cis-trans conjugated bonds at any time in the course of polymerisation. This is easily understood as the formation of conjugated double bonds is slow process, whereas their interaction in the polymerisation process is comparatively a fast process.[51] Therefore, in most of the cases, only the absorption peak due to isolated trans i.e. 10.34 micron is observed.

The main fatty acid components of linseed oil are linolenic and linoleic acids. Wheeler[53] studied the thermal polymerisation of esters of linoleic and linolenic acids by adsorption in the region of 10 micron to explain dimer and trimer formation. In linoleic ester cis-trans conjugated isomers were found to polymerise about six times as rapidly as non-conjugated compounds and trans-trans conjugated isomers polymerise five times as fast as the cis-trans conjugated isomers. Linolenates react in a similar manner but the rate of polymerisation is much more rapid.

In some cases peak due to cis-trans conjugated namely, 10.53 micron is seen when its polymerisation is taking place at a slow rate i.e. when butyl titanate is not present. But no peak is observed due to trans-trans isomer i.e. 10.12 micron as this configuration can

polymerise very rapidly. The fact that the heated oil shows existence of large number of isolated trans bonds indicates the possibility of the formation therefore of conjugated trans-trans bonds; but these bonds are not shown because they disappear immediately on polymerisation due to saturation. On continued heating the 10.34 micron bonds first increase in intensity and then decrease.

In view of the conjugated trienes not indicated in the ultraviolet studies, their absence in the infrared spectra may be explained as being due to their polymerisation as soon as these are formed.

Ultraviolet Absorption: The ultraviolet spectrophotometry has been used for analysis of the conjugated dienes and trienes. These are determined from the optical density of linseed oil heated without butyl titanate and with 0.1 to 0.6 percent of butyl titanate for ten hours at 233 millimicron and 268 millimicron (Table 16).

Table 16

Diene and triene conjugation in linseed oil heated in presence of butyl titanate at 250°C for 10 hours

Butyl titanate wt. % of vol. of oil	Optical density at 233 milli-micron	Diene conjugation %	Optical density at 268 milli-micron	Triene conjugation %
0.0	0.25	27.14	0.205	0.41
0.1	0.2875	31.05	0.1375	0.28
0.2	0.3625	39.15	0.06	0.12
0.3	0.305	32.94	0.0875	0.18
0.4	0.2875	31.05	0.1925	0.29
0.5	0.1825	19.71	0.0875	0.18
0.6	0.0975	10.53	0.015	0.03

the proportion of triene conjugation is negligible whereas the proportion of diene conjugation is 30 percent for the oil heated alone and with 0.1 to 0.4 percent butyl titanate. For higher proportions of butyl titanate the proportion of the conjugated double bonds at this stage of reaction is less. On examination of the data in the light of the earlier discussion under infrared studies, it will be seen that the conjugation is entirely made of cis-cis configuration which is not shown in the infrared and due to steric hindrance is polymerised very slowly. Paschke and Wheeler[45] have given polymerisation rates for different cis-trans conjugation and non-conjugated configuration (Table 10) and have reported that the rates with trans-trans conjugated double bonds are 20 to 25 times greater than those for isolated trans. It would appear from the preponderance of the cis-cis conjugation in the product even after ten hours of polymerisation that the rate of polymerisation of cis-cis conjugation is lower than that of the isolated trans double bonds.

Refractive index: The readings taken with linseed oil heated with and without butyl titanate for 16 hours (Table 17) show the same refractive index for linseed oil heated alone and with 0.1, 0.2 and 0.3 percent butyl titanate. With higher proportions of butyl titanate it diminishes with the increase in the butyl titanate added. If refractive index values are considered as an indication of the double bonds present in the system as suggested

Table 17

Change in refractive index on heating linseed oil at 250°C in presence of butyl titanate

Butyl titanate wt. % on vol. of oil	Refractive Index after hours.							
	1	2	4	6	8	10	12	16
0.0	1.4770	1.4772	1.4782	1.4800	1.4790	1.4820	1.4810	1.4830
0.1	1.4770	1.4780	1.4790	1.4800	1.4810	1.4804	1.4815	1.4830
0.2	1.4775	1.4780	1.4785	1.4790	1.4805	1.4815	1.4820	1.4830
0.3	1.4770	1.4770	1.4760	1.4780	1.4785	1.4850	1.4810	1.4830
0.4	1.4770	1.4775	1.4765	1.4780	1.4785	1.4793	1.4810	1.4825
0.5	1.4760	1.4750	1.4760	1.4780	1.4780	1.4797	1.4810	1.4815
0.6	1.4760	1.4650	1.4650	1.4780	1.4790	1.4796	1.4815	1.4816

by Waterman and others[57,58], it will mean that the number of double bonds on addition upto 0.3 percent butyl titanate is same. However, it is seen that the extent of polymerisation as indicated by the viscosity readings varies considerably with the amount of butyl titanate added. This observation supports the earlier statement that the polymerisation in some cases takes place only with dimer formation, in other cases trimers and higher three dimensional polymers are formed. Butyl titanate in optimum proportion accelerates the process, but with higher or lower proportions of butyl titanate there is a tendency to saturate the double bonds by dimer or trimer formation and viscosity increase is correspondingly less.

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PART III

APPLICATION OF BUTYL TITANATE IN THERMOSTABLE AND THIXOTROPIC PAINTS

I N T R O D U C T I O N

Butyl titanate promotes adhesion. Thin films of titanium dioxide deposited from dilute solutions of butyl titanate enable films of paints, lacquers, etc. to be applied much more effectively to a very wide range of surfaces. Modifiers like paraffin wax, napthene, glycols and aliphatic alcohols are added to retard hydrolysis which helps formation of thin films.

Thermostable coating

Butyl titanate is also used in heat resistant paints.[59] The paints consist of aluminium and butyl titanate. When such a paint is applied to a surface, butyl titanate is hydrolysed by atmospheric moisture and during subsequent heating is converted to titanium dioxide. The function of titanium dioxide formed from butyl titanate is to improve the adhesion and protection of the aluminium film. After exposure to high temperature, the paint film becomes hard and sticks to the underlying steel. The maximum temperature at which butyl titanate/aluminium paint is serviceable is about 600°C. Since melting point of aluminium is 660°C, above this temperature the paint film affords protection for a limited period but can not be regarded as very satisfactory. One defect of butyl titanate/aluminium coating is its comparatively poor resistance to atmospheric corrosion. This tends to limit its application to outdoor surfaces which are hot for most of the time. Butyl titanate/zinc paint, on the other

hand has considerable resistance to atmospheric corrosion. This improvement is only gained at the expense of decreased resistance to temperatures above 400°C. However, by using a zinc pigmented coating followed by another coating of butyl titanate/aluminium paint, protection from atmospheric and heat corrosion is obtained at higher temperature also.

Many silicone resins are cured at temperatures upto 250°C.[60,61] This is of course no disadvantage when used as a heat resistant finish, but it limits the applications of such paints to materials which can not be heated to these temperatures. More particularly it prevents the attainment of the best effect when silicones are applied to textiles, leather, etc. to obtain a water repellant finish. The addition of butyl titanate decreases the time and temperature required for curing these resins.

Small addition of butyl titanate to a paint formulation controls the rate of oxidation of drying oils and is therefore capable of prolonging the life of paint films. The presence of 1 to 2 percent butyl titanate improves the gloss and colour retention of paint. This effect seems to be due to the ability of butyl titanate to control chalking.

Thixotropic paints

For the purpose of paint technology, thixotropy means that paint has a viscosity which is fairly high when the system is at rest and which falls to a much lower

value under an applied shear stress such as may be produced by shaking or stirring and then recovers during subsequent standing.

Thixotropic paints as sold are solids, but under the shearing action of painting process they change to liquids which are easily brushable but after some time again solidify, thus reducing curtaining and running. Freedom from curtaining and running is achieved by the fully thixotropic nature, the paint being broken down from its jelly like state by agitation under the brush. A finite time is taken to revert to the original state. This time, a few minutes, is long enough to allow good flow but not long enough to allow the formation of curtains or runs thus giving truer colours. Thixotropic paint is much more easily brushed than usual decorative finishes as layer brush loads can be transferred from the tin to the working surface where the true viscosity of the paint is attained by shear under the brush.

These properties give particular sales appeal to a paint but from a technical point of view also it is improved especially by prevention of settlement.[62] Due to thixotropic state of the material a fairly rigid gel is maintained in the can restricting the downward movement of heavy pigments under the influence of gravity, a homogeneous blend is therefore maintained. Shelf life is also greatly increased compared with conventional paints, without the tedious necessity of inverting tins periodically. Exposure tests have shown that paints based on

thixotropic material have excellent exterior durability. It has been observed that addition of butyl titanate improves the dispersion of pigment and thixotropy of the paint formulation.[63]

Thus butyl titanate finds use in many industries. The present study deals only with application of butyl titanate (1) in thermostable coating and (2) for improvement in dispersion of pigment and thixotropy of typical titanium dioxide linseed oil paints.

M E T H O D S

Thermostable coating

Panels of 30 x 10 x 0.1 cm. were cut from mild steel sheet, treated with dilute sulphuric acid, dried and cleaned with sand paper till a smooth surface was obtained. The panels were then further treated with dilute phosphoric acid, dried and used.

The panels were painted with the paint formulation consisting of 6 parts of aluminium paste, 2.5 parts white spirit and varying amounts of butyl titanate from 0 to 6 parts. The painted panels were kept exposed to atmosphere for 3 days and then heated to 600°C directly with a burner in the 'REL' fire retardance apparatus. This apparatus consists of an open fronted oven approximately 45 x 30 x 30 cm. constructed in fire-proof insulating board. Two runners are provided to hold the panel vertical and circular gas burner, adjustable in relation to the panel, is fitted to the lid.

The gas burner was adjusted to 2.5 cm. from the panel and the flame adjusted with air and gas mixture, to give a temperature of about 600°C. The air and gas pressures were kept constant throughout the test. The flame was directed on to the panel at the commencement of each test by rapidly withdrawing the asbestos screen and allowed to play on the panel for 2 minutes.

Dispersion

Hegman Grind Gage was used to study fineness of pigment particles and uniformity of its dispersion in paints.

The instrument consists of a wedge shaped channel 1/2 inch wide and ranging from 0 to 0.005 inches deep, cut in a hardened tool steel block and a linear scale beginning with zero where the channel is 0.005 inches deep etched along side the channel. To evaluate the fineness of grind, gage is laid flat, and the deep end is slightly overflowed with the paint. Holding the scrapper perpendicularly on the gage and using firm pressure, the paint is drawn towards the shallow end of the channel. The drawdown at grazing incidence where the coarse particles appear on the surface of the film, is noted, disregarding occasional particles in the deeper end.

The paint consisted of 50 g. pigment and 100 g. alkali refined linseed oil. The pigments used were (1) rutile, (2) anatase, (3) calcium plumbate, (4) barium potassium chromate, (5) cadmium sulphide and (6) lithopone.

The amount of butyl titanate was varied from 0 to 1.0 percent on the weight of linseed oil. Butyl titanate was added as 25 percent solution in xylene and the amount of xylene was kept constant in each case by adding excess amount of xylene.

The paints were prepared in a cylindrical bottle of 500 ml. capacity with bakelite pilfer-proof lid and were mixed on roller mill by means of 50 g. porcelain balls (8 mm. dia.). As after shaking for 6 hours, the dispersion does not increase to any appreciable extent, 6 hours shaking was taken as standard to study thixotropy.

Thixotropy

Paints consisting of 50 g. of pigment and 100 g. of alkali refined linseed oil were prepared with additions of 0 to 1.5 percent butyl titanate. The bottle was transferred to a roller mill and shaken for 6 hours to ensure homogeneous mixing. The paint was immediately transferred to the Stormer's Viscometer and change in viscosity at intervals of 30 minutes was determined. Increase in viscosity was taken as an index of gel formation.

For determining the gel to sol transformation, the paint was gelled by mixing in roller mill for 6 hours as described above and then keeping undisturbed for 16 hours. The viscosity of the gel was then determined. The gel was transformed to sol by shaking and the sol formation was followed at intervals of 30 minutes by decrease in the viscosity.

RESULTS AND DISCUSSION

Thermostable coating

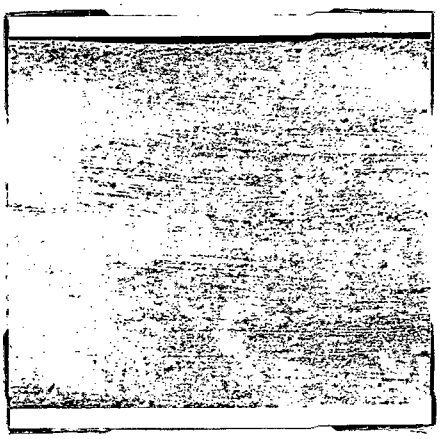
Blister formation and ignition of the paint films were observed while it was being heated. Photographs of selected panels were taken after cooling. Before the panel was exposed to high temperature, while the paint film containing butyl titanate adhered well to the panel surface, the film without butyl titanate could be removed even by touching. On heating the panel to 600°C the adhesion was not improved when butyl titanate was not present and the film came out exposing the panel surface as can be seen from the photographs (Fig. 28). It was observed that with a panel painted with formulation containing butyl titanate, the paint film became extremely hard and so adherent that its removal was not possible without injury to the underlying steel. It was also observed that increase in butyl titanate more than one part does not further improve the adhesion and stability of the paint film towards heat.

Dispersion

The results of the studies with Hegman Grind Gage are given in Tables 18 and 19. It will be seen that the dispersion of calcium plumbate is complete in about 6 hours in absence of butyl titanate. Addition of the titanate reduces the time for completion of dispersion from 6 hours to 4 hours. There is slight improvement in dispersion

(1)

(2)



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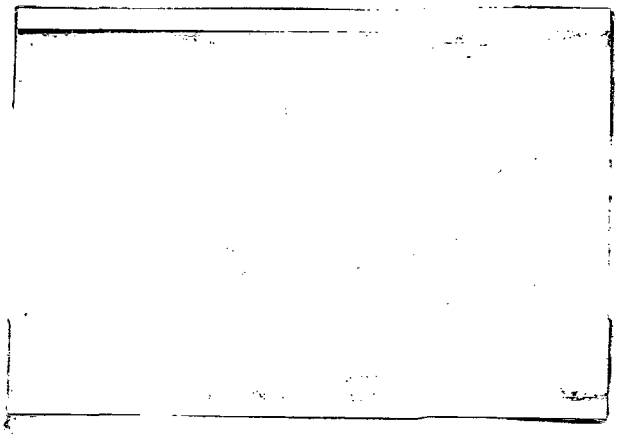

Fig. 28. Panels showing effect of heat on aluminium paint in presence of (1) nil, (2) 0.1, and (3) 0.3 parts butyl titanate.

Table 18

Fineness of pigments in paint with butyl titanate

Pigment	Reading on Hegman Grind Gage after 6 hours mixing of the paint in butyl titanate, % by weight of linseed oil.										
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Calcium plumbate	8	8	8	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5
Rutile	3	3.5	4.5	4.5	7	8	8	8	8	8.5	8.5
Anatase	2	2.5	3.5	4	6	7.5	7.5	7.5	8	8	8
Cadmium sulphide	3.5	3.5	4	4	5	5	5.5	5.5	6	6	6
Lithopone	Nil	1	1	1.5	2	2	2.5	3	3	3	4
Barium potassium chromate	Nil	1	1	1	1.5	1.5	1.5	1.5	2	2	2.5

Table 19

Fineness of pigments in paint with nil, 0.2, 0.5 and 0.8 % butyl titanate varying time of mixing

Pigment	Reading on Hegman Grind Gage for paint with butyl titanate after mixing for															
	2 hrs	4 hrs	6 hrs	8 hrs	2 hrs	4 hrs	6 hrs	8 hrs	2 hrs	4 hrs	6 hrs	8 hrs	2 hrs	4 hrs	6 hrs	8 hrs
	0.0% butyl titanate				0.2% butyl titanate				0.5% butyl titanate				0.8% butyl titanate			
Calcium plumbate	5.5	6	8	8	7.5	8	8	8	7.5	8	8	8	7.5	8	8.5	8.5
Rutile	Nil	2	3	3	3.5	4	4.5	4.5	4	6	8	8	4.5	7.5	8	8
Anatase	Nil	1	2	3	1.5	3.5	4	4.5	4	5.5	7.5	7.5	4	6	8	8
Cadmium sulphide	Nil	2	3.5	4.5	1.5	2.5	4	4	2.5	4	5.5	6	3	5	6	6.5
Lithopone	Nil	Nil	Nil	Nil	1	1	1	1	1	1.5	2.5	2.5	1	2.5	3	3
Barium potassium chromate	Nil	Nil	Nil	Nil	1	1	1	1	1	1	1.5	2	1	1.5	2	2

by increasing the amount of the titanate. Cadmium sulphide shows similar results but the fineness of the pigment being less the reading on the gage is 6 to 6.5 instead of 8 to 8.5 for calcium plumbate. Also amount of butyl titanate required is higher, namely, 0.8 percent on the weight of linseed oil. Lithopone and barium potassium chromate are not dispersible without butyl titanate. The dispersion is slightly increased in presence of butyl titanate and with increase in the time of mixing. Rutile and anatase paints show accelerated dispersion in presence of butyl titanate. The rutile paints show greater dispersion than anatase paint under similar conditions. For getting dispersion to the same extent higher proportions of butyl titanate and longer periods of mixing are required in case of anatase. In the subsequent study on thixotropy, therefore only anatase and rutile paints were used. The time of mixing was kept constant for 6 hours.

Thixotropy

It is seen from Table 20 and Fig. 29 that the viscosity of the paint decreases with increase in time of mixing keeping butyl titanate same and also decreases with increase in proportion of butyl titanate added using the same time for mixing.

The decrease in viscosity is linear. The rate of decrease in viscosity is slowed down when the equilibrium value is neared. This is reached earlier in case

Table 20

Relationship between time of mixing and viscosity of paint

Time in Hours	Viscosity in centipoises of rutile paint		Viscosity in centipoises of anatase paint	
	Butyl titanate % on the weight of oil		Butyl titanate % on the weight of oil	
	0.25	0.5	0.25	0.5
1	180.5	155.3	226.5	172.0
2	161.5	126.0	212.0	144.0
3	149.0	100.0	190.0	125.0
4	137.0	83.0	178.0	107.5
5	119.5	64.0	160.5	95.0
6	109.0	64.0	142.5	87.3
7	100.0	-	130.0	83.3
8	91.5	-	125.0	81.0

of rutile and also with higher proportion of butyl titanate. In case of anatase and with lower proportions (0.25%) of butyl titanate the linearity is shown even upto 8 hours.

The viscosity value with 0.5 percent butyl titanate after 3 hours is same as the viscosity value with 0.25 percent butyl titanate after 7 to 8 hours both for rutile and anatase indicating that the sol formation is faster with higher proportion of the titanate.

Keeping the time of mixing constant (6 hours)

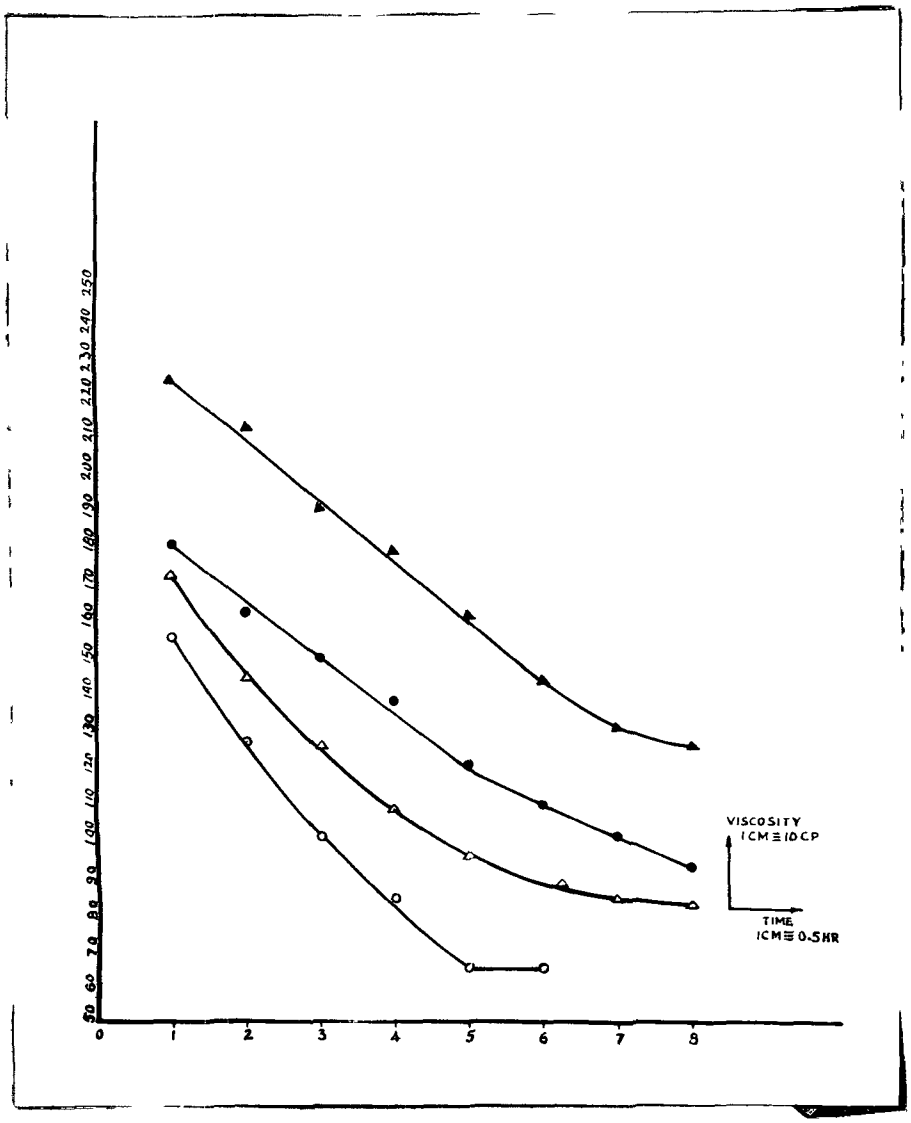

Fig. 29. Relationship between time of mixing and viscosity of paint in presence of (1) rutile paint with △- 0.25, ⊙-0.5 percent butyl titanate and (2) anatase paint with ▲- 0.25, and ●- 0.5 percent butyl titanate.

the viscosity of the paint was determined varying butyl titanate (Table 21; Fig. 30). The viscosity decreases with increase in butyl titanate. This is true both for rutile and anatase.

Table 21

Effect of butyl titanate on viscosity of paints

Pigment	Viscosity in centipoises				
	Butyl titanate % on the weight of oil				
	0	0.25	0.5	1.0	1.5
Rutile	220.0	110.0	64.5	64.0	63.0
Anatase	279.5	144.0	88.3	79.3	72.3

By addition of only 0.25 percent butyl titanate viscosity is decreased to half of its value for the paint without butyl titanate. With addition of 0.5 percent butyl titanate there is proportionate decrease in viscosity. However, on addition of butyl titanate in proportions higher than 0.5 percent further decrease is negligible. Thus in case of rutile paint with 0.5 percent butyl titanate the viscosity is 64.5, with 1.0 percent it is 64 and with 1.5 percent, it is 63 centipoises. For anatase the values for viscosity are 88.3, 79.3 and 72.3 centipoises for similar amounts of butyl titanate.

The result of study of sol to gel transformation by keeping anatase and rutile paints in presence of 0.25, 0.5, 1.0 and 1.5 percent butyl titanate undisturbed

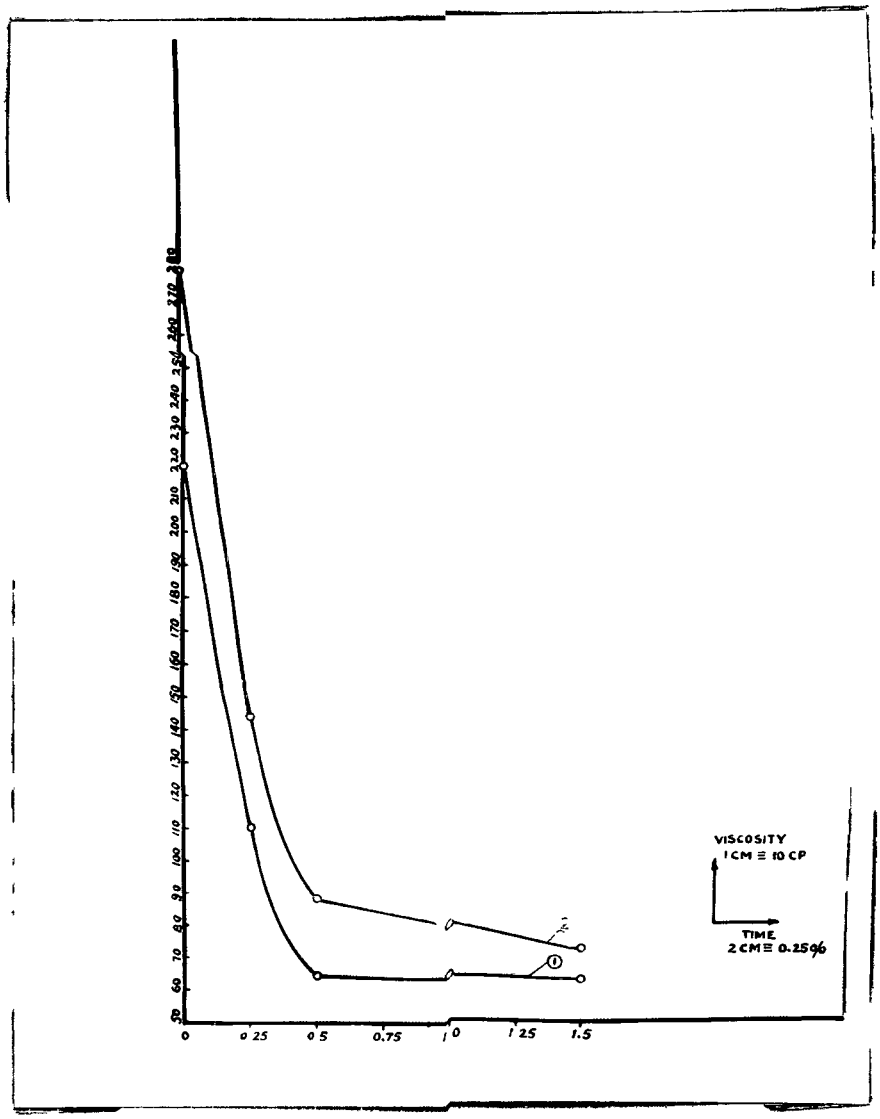

Fig. 30. Relationship between viscosity and amount of butyl titanate of (1) rutile and (2) anatase paints.

which was followed by viscosity measurement is given in Tables 22 and 23 and shown in Figs. 31 and 32.

Table 22

Sol to gel transformation of anatase paint in presence of butyl titanate.

Time in Hours	Viscosity in centipoises			
	Butyl titanate % on the weight of oil			
	0.25	0.5	1.0	1.5
0.0	144.0	86.3	79.3	72.3
0.5	144.0	88.3	79.3	72.3
1.0	144.0	88.3	80.5	74.3
1.5	144.0	89.8	82.0	79.0
2.0	145.5	91.8	85.5	89.8
2.5	145.5	95.0	95.0	102.8
3.0	146.5	100.0	104.5	110.0
3.5	148.0	105.8	113.0	120.3
4.0	148.0	112.0	123.5	130.0
4.5	150.0	119.8	132.0	141.0
5.0	151.5	130.0	142.5	149.0
5.5	151.5	131.3	151.5	159.0
6.0	154.0	145.5	160.0	172.0
6.5	155.5	154.0	170.5	184.5
7.0	156.5	161.5	180.5	192.5
7.5	159.0	168.0	192.0	202.5
8.0	164.0	178.0	205.5	214.5

Table 23

Sol to gel transformation of rutile paint in presence of butyl titanate

Time in Hours	Viscosity in centipoises			
	Butyl titanate % on the weight of oil			
	0.25	0.5	1.0	1.5
0.0	110.0	64.5	64.0	63.0
0.5	110.0	66.5	66.5	68.8
1.0	112.5	70.3	71.5	70.3
1.5	112.5	84.8	82.0	83.3
2.0	114.0	97.0	100.0	100.0
2.5	116.0	121.8	119.8	115.0
3.0	117.8	140.0	140.0	142.5
3.5	122.3	158.0	161.5	160.0
4.0	127.0	180.5	180.5	178.0
4.5	132.6	200.0	200.0	199.0
5.0	142.5	225.0	221.0	221.0
5.5	154.0	233.0	241.0	238.0
6.0	164.0	252.5	256.0	260.0
6.5	175.5	278.5	278.5	279.5
7.0	188.5	294.0	290.0	299.0
7.5	202.5	318.0	315.0	315.0
8.0	215.5	332.0	329.0	340.0

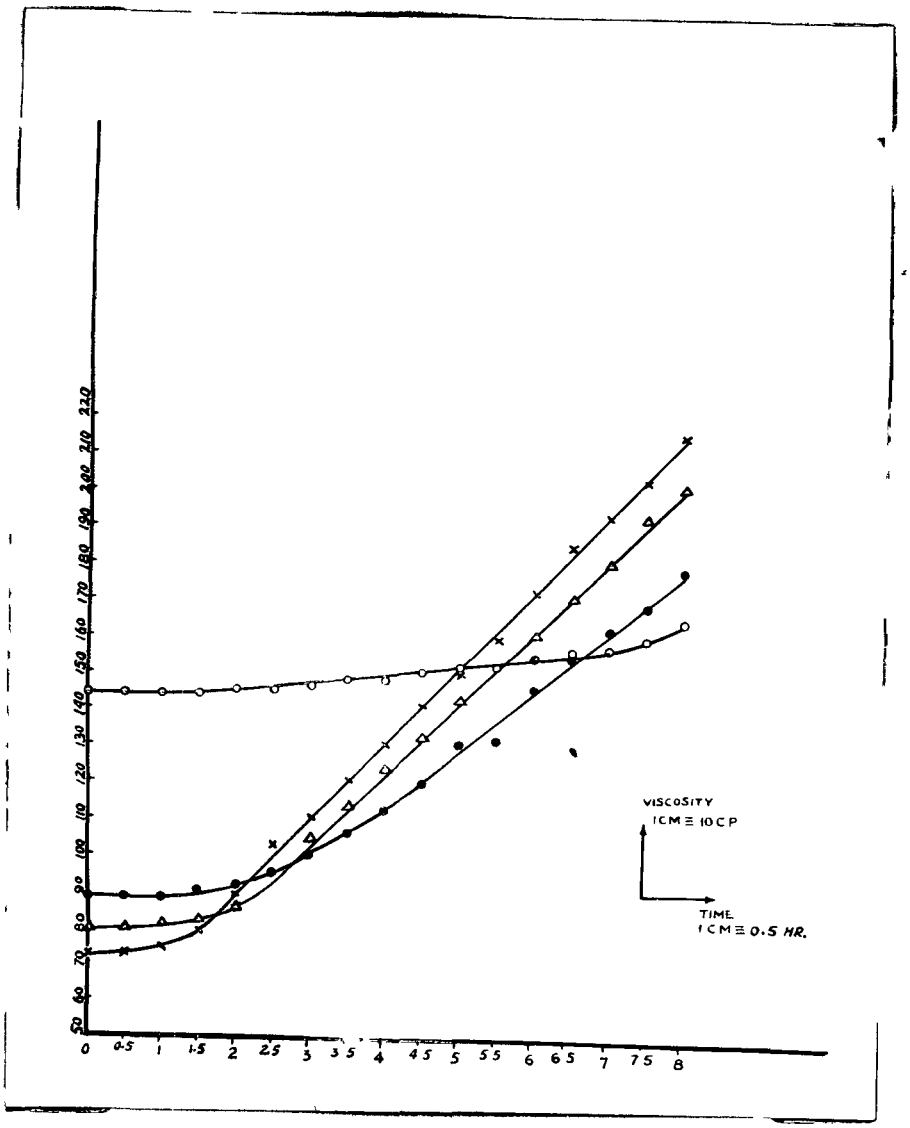

Fig. 31. Sol to gel transformation of anatase paint in presence of ⊙- 0.25, ●- 0.5, △- 1.0 and ×- 1.5 percent butyl titanate.

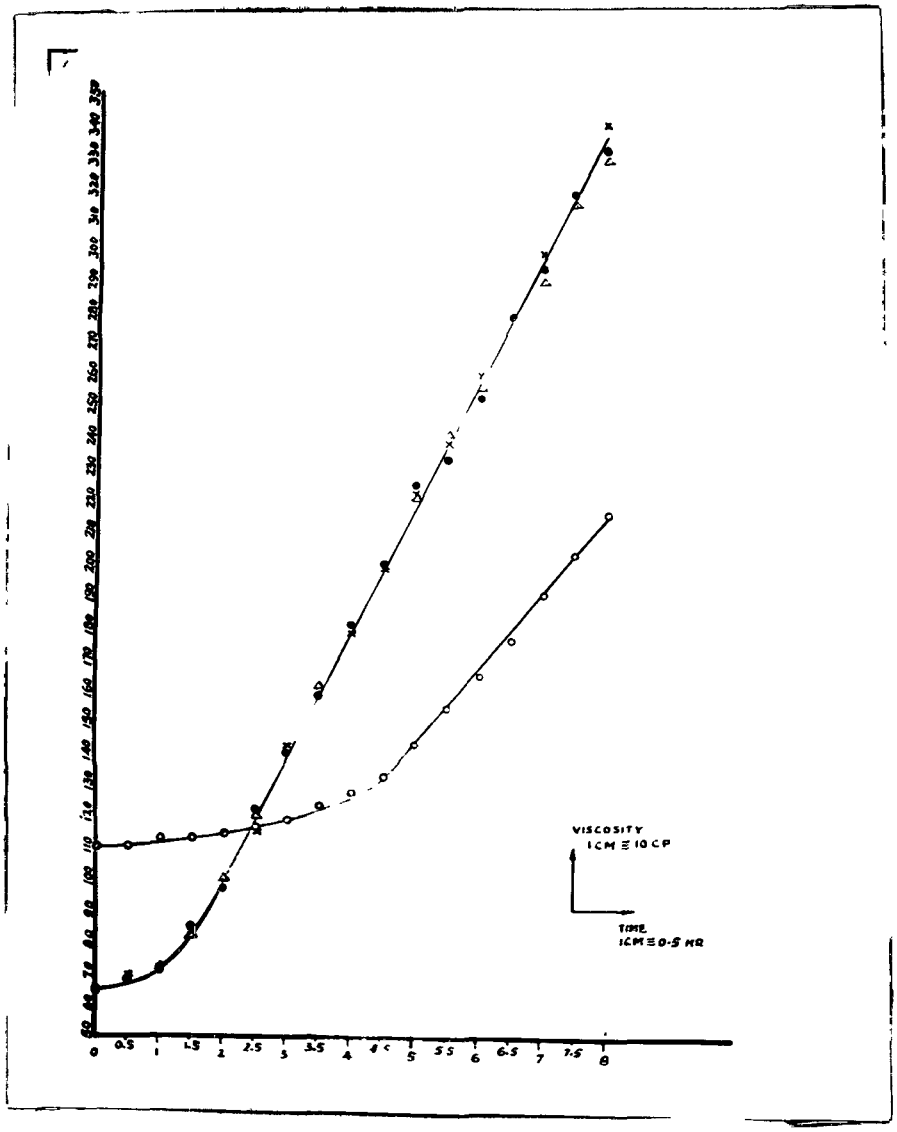

Fig. 32. Sol to gel transformation of rutile paint in presence of ⊙- 0.25, ●- 0.5, △- 1.0 and ×- 1.5 percent butyl titanate.

For a particular concentration of butyl titanate, the viscosity of the paint increases with time of keeping. At lower concentration of butyl titanate the increase in viscosity is not appreciable. With higher concentrations of butyl titanate, the initial viscosity is low but the viscosity increases more quickly. For example, with 0.25 percent butyl titanate the initial viscosity is 144 centipoises, after 4 hours it is 148 and after 8 hours it is 164; with 0.5 percent concentration of butyl titanate initially it is 88.3, 112 after 4 hours and 178 after 8 hours and with 1.5 percent butyl titanate it starts with 72.3, after 4 hours it is 130 and after 8 hours it is 214.5 centipoises.

By increasing the butyl titanate concentration, certain viscosity value such as 160 centipoises can be attained in less time. Thus for example, for anatase paint, this viscosity for 0.25 percent butyl titanate concentration is shown in 7.5 hours, for 0.5 percent concentration in 7 hours, for 1.0 percent concentration in 6 hours and for 1.5 percent concentration in 5.5 hours, although the initial viscosities at higher concentrations of butyl titanate are lower. In case of rutile paint, however, the viscosity remains almost constant after the addition of butyl titanate in proportions higher than 0.5 percent. The change in the viscosity is shown when the amount of butyl titanate

is upto 0.5 percent. The plots of viscosity against time are linear and for 0.5, 1.0 and 1.5 percent butyl titanate are overlapping.

The gel thus formed by keeping the system undisturbed can again be brought into sol form by stirring and shaking (Table 24, Fig. 33). The sol

Table 24

Gel to sol transformation of rutile and anatase paints in presence of butyl titanate

Time in Hours	Viscosity in centipoises of rutile paint		Viscosity in centipoises of anatase paint	
	Butyl titanate % on the weight of oil		Butyl titanate % on the weight of oil	
	0.25	0.5	0.25	0.5
0.0	332.0	530.0	178.0	199.0
0.5	278.5	278.5	171.5	151.5
1.0	115.0	64.0	168.0	142.5
1.5	80.0	64.0	165.5	127.5
2.0	-	-	160.0	115.0
2.5	-	-	154.5	104.5
3.0	-	-	151.5	95.0
3.5	-	-	142.5	85.5
4.0	-	-	141.0	82.0

formation as indicated by decrease in viscosity is higher in case of rutile than anatase. The initial

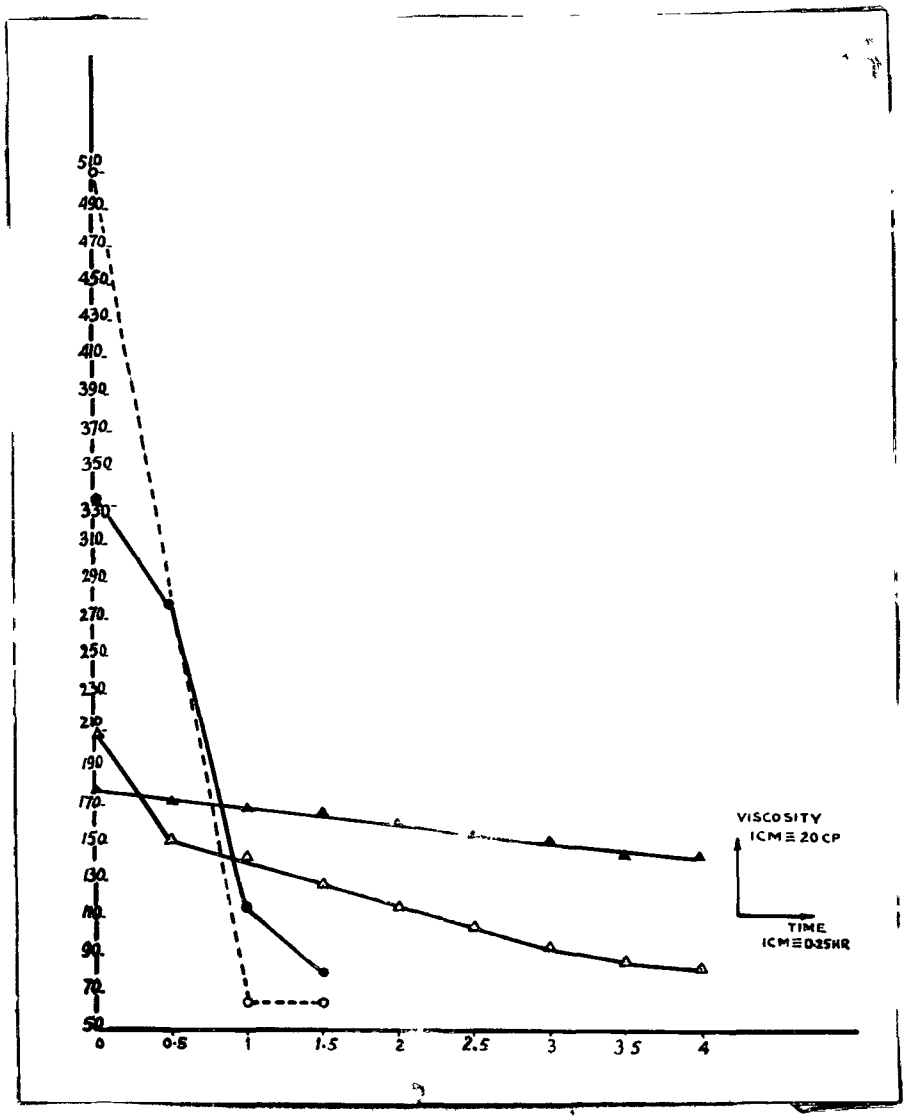

Fig. 33. Gel to sol transformation of (1) rutile paint with ●- 0.25 and ⊙- 0.5 percent butyl titanate and (2) anatase paint with ▲- 0.25 and △- 0.5 percent butyl titanate.

viscosity reading for anatase gel with 0.25 percent butyl titanate is lower than that with 0.5 percent butyl titanate. The decrease in viscosity that is sol formation is gradual but is accelerated to a great extent by increase in butyl titanate. The same viscosity value is attained by the gel in 0.5 and 1 hour with 0.5 percent titanate and in 2.5-3 and 3.5 hours with 0.25 percent butyl titanate.

The drop in viscosity in case of rutile is sudden. Although initial viscosity with 0.25 and 0.5 percent butyl titanate is different, e.g. 332 and 530, the viscosity value attained after 0.5 hours is same in both the cases, that is 278.5 centipoises, but after 1 hour again these differ, 115 and 64, the latter being equilibrium value. There is no further decrease in viscosity with the paint containing 0.5 percent titanate while the paint with lower titanate content attains the equilibrium value for viscosity rather slowly.

Factors affecting thixotropy: Thixotropy was first defined by Peterfi[64] as an isothermal reversible sol/gel/sol transformation. The word thixotropy means change by touch indicating that the material decreases in viscosity on shear but builds up again when at rest. More recently the definition of thixotropy has been broadened to include materials which exhibit an isothermal reversible transformation from a higher to a

lower viscosity gel. It has also been found that this transformation can be brought about by an increase in rate of shear followed by rest period or by the application of a constant rate of shear over a period of time followed again by a rest period.

Freundlich[65] describes a thixotropic material as one that will undergo isothermally a gel/sol/gel transformation but has qualified this definition by pointing out that the conversion to a complete sol is a specially characteristic and limiting case of thixotropy. This permits paints to be classified as thixotropic. A complete transformation of a gel to true sol is not a prerequisite for thixotropy, a partial transformation is all that is necessary.[66,67]

Today we know that suspensions of pigments in non-aqueous media such as oil paints also exhibit thixotropy. It is a fact that our knowledge of thixotropy in its true sense has been derived mainly from the study of paints.

Thixotropy is one of the four forms of non-Newtonian viscosity, e.g. thixotropy, false body, anamalous viscosity, dilatamy and rheopexy. Only the first three types concern paint systems. In case of thixotropy the rate of shear increases with shear stress initially but after sometime there is a fall in shear rate although the shear stress increases. In addition time also plays an important part in this phenomenon.

Unlike other types of viscosities wherein adjustment of shear rate and shear stress takes place simultaneously, appreciable time is required for the viscosity of thixotropic system to fall when increase in shear stress has ceased. In a truly thixotropic system, when no physical or chemical changes occur, reversal of stress can be imposed on the system on numerous successive occasions separated by long intervals of time without altering the path of the stress-strain relationship.

When we consider the physical basis of thixotropy, the existence of shear stress even when the system is at rest, the fall in shear stress when shear rate is increased and the time lag between the removal of the shear stress and recovery of the system to its original viscosity have to be kept in mind because all these features together make thixotropy.

For a system which is affected by shear stress some sort of structure has to be supposed.[68] For thixotropic behaviour the form of structure postulated consists of loose cage-like structure uniting the particles and enclosing the liquid vehicle which is a gel and possesses rigidity and elasticity. According to Green[67] the suspended particles are usually of pigment and in some cases polymerised molecules of vehicles like linseed oil may also take part in structure building.

Changes in electrical condition of the pigment particles which is created due to the irregularity of their shape is another important aspect affecting the system. In addition the surface active agents and electrolytes have considerable effect on the thixotropic behaviour due to opposite electrical charges created as a result of asymmetry in their shape, thus particle shape plays an important part in thixotropy. Therefore, the conditions which change the size and shape of the particle can also alter the degree of thixotropy. An interesting example is the change in the thixotropic behaviour of lithopone when it is calcined at various temperatures due to increase in particle size.

When a shear stress is applied to such a system wherein due to opposite forces the particles are held together, the particles reorientate themselves into a new alignment and a shift appears in their resistance to flow. Goodeve[69] suggests that since the thixotropic system possesses a loose structure shear stress causes the links in the structure to be stretched and broken and after sometime the structure is recovered to its original position due to Brownian movement which brings the particles into contact again and original equilibrium is re-established. The time lag between the recovery of the system to its original condition and removal of stress is thus explained. Green's theory

also explains the gel-sol transformation.

Similar to the effect of shape the surface active agents are also responsible for modifying the nature and magnitude of the forces working between the pigment particles. Addition of small amounts of such agents can have a profound effect on the thixotropic behaviour of suspensions in various media specially paint formulations. In a non-aqueous medium, which is also non-polar, the particles of the medium and suspended pigment tend to repel each other. The surface active agents when present in such a system encourage the particle of medium and pigments to merge with each other and the required structure for thixotropy is created. Water, when added in the form of solution of electrolyte or soap, is adsorbed on the surface of the pigment and sets up a high interfacial tension with the vehicle thus causing the particles to be joined into a continuous desired structure. Thus pigment particles play an important role in the structure formation. The structure is further affected by orientation of sizes and shape and concentration of the particles.

Many attempts have been made to specify thixotropy by some coefficient. The main difficulty lies in the fact that for many systems, the process required to make the measurements causes the breakdown to proceed and there are therefore no steady states. In some systems it is claimed that a steady state of stress can be reached

at constant rate of shear[70] and many papers by Green and Weltmann[67] in which case thixotropy can be measured either analogously to a yield-value or in terms of the loss in shearing stress per unit increase in velocity gradient in unit time. Much misunderstanding in the past has undoubtedly been caused by failure to realise how many and deverse phenomena are to be found under the general heading of thixotropy. In some, the extent of the breakdown is primarily a function of the magnitude of the stress, in other the amount of shear and in others again, perhaps, the rate of shear which is no simple function of stress.[71,72]

Goodeve and Whitfield[70] have shown that there is a linear relationship between apparent viscosity and reciprocal shear rate which could be expressed by the function

$$\eta = \eta_0 + \frac{\phi}{V}$$

where η_0 = residual viscosity at nil shear
V = reciprocal shear rate
ϕ = coefficient of thixotropy, i.e. slope of the curve of apparent viscosity which cuts the viscosity axis at that value.

Arnold[73] examined the effect of these factors on Goodeve's coefficient of thixotropy for suspensions of carbon black in non-polar paraffin and found to be almost independent of temperature. In United States Stormer and and McMichael viscometers have long been popular for the testing of paints and for non-Newtonian viscosity behaviour.

Suggested mechanism of thixotropy in presence of butyl titanate

To explain thixotropic behaviour of a system, it is necessary to visualise the mechanism of the gel to sol and sol to gel transformation under stress in the system. The system when at rest is gel, on disturbing it becomes sol which upon standing again forms a gel. The prerequisite for a thixotropic system is gel formation. The gel formation in case of thixotropic system takes place when the liquid is trapped between particles of solid and loses its mobility and the system becomes viscous.

In the system under study rutile or anatase is dispersed in the linseed oil medium. The resulting sol is unstable and on keeping, the pigment quickly settles down. When butyl titanate is added to such a system it gets adsorbed on the pigment particles. A portion of butyl titanate hydrolyses to form butyl alcohol and titanium hydroxide. Freshly precipitated titanium hydroxide is more reactive than the titanium dioxide pigment and helps in stabilisation of the titanium dioxide sol.

Butyl titanate also induces the gel formation, the possible mechanisms are: (1) the adsorbed titanate sets up a high interfacial tension with linseed oil forming a continuous structure, (2) butyl titanate dissociates weakly into butyl and titanate ions; the titanate

ions are adsorbed on the pigment particle while the butyl ions have affinity for the oil and remain dispersed in linseed oil. Due to weakly dissociating nature of butyl titanate, butyl ions are not very far removed from the titanate ions. The butyl ions together with the oil molecule with which they are associated remain in the neighbourhood of the pigment particles. Thus butyl titanate acts as a link between pigment and vehicle oil. Owing to the tetravalent nature of titanium ion, at least four linseed oil polymolecules are associated with each pigment particle when only one butyl titanate molecule is adsorbed on a pigment particle. The linseed oil thus is immobilised and the system becomes more and more viscous.

When the system is disturbed by stirring or shaking the titanate and butyl ions are separated and linseed oil regains its mobility, the viscosity decreases and the system shows gel to sol transformation. About 0.5 percent butyl titanate is required for the gel formation. With addition upto 0.5 percent the gel formation is accelerated as shown by the increase in viscosity. With addition of higher proportions the rate of increase of viscosity that is the rate of gel formation is same as that when 0.5 percent butyl titanate is added. The minimum requirement of the titanate is one molecule for each polymerised molecule of linseed oil.

The optimum composition for gel formation is 100 parts of linseed oil, 50 parts of pigment and 0.5 parts of butyl titanate, which is in agreement with the above.

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